Metal-assisted Cycloadditions. Part 2.† Reactions of Dicarbonyl(η^5-cyclopentadienyl)(η^1-3-methoxyallyl)iron with Electron-deficient Olefins and Acetylenes

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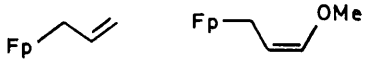
Dicarbonyl(η^5-cyclopentadienyl)(η^1-3-methoxyallyl)iron has been treated with ethyl 3,3-dicyanoacrylate, diethyl 1-cyanoethylenedicarboxylate, ethyl 2,3-dicyanoacrylate, diethyl methylenemalonate, and trimethyl ethylenetricarboxylate to yield the corresponding cyclopentyl–Fp derivatives [Fp = $Fe(CO)_2$(cyclopentadienyl)] as a mixture of diastereoisomers and these have been separated by column chromatography. The Fp-moiety of these cyclopentyl-Fp adducts has been replaced with an alkoxycarbonyl group by treatment with ceric ammonium nitrate. Substituted cyclopentene derivatives have been isolated from the reaction of these Fp-adducts with either hydrogen chloride or trityl tetrafluoroborate.

REACTION of (η^1-allyl)dicarbonyl(η^5-cyclopentadienyl)-iron (1) with tetracyanoethylene [1] and a variety of other electrophilic, unsaturated moieties [2-7] has been shown to yield cyclopentanoid derivatives *via* a cycloaddition process. In the preceding paper we reported [8] the reactions of complex (1) with a number of cyano- and alkoxycarbonyl-substituted alkenes and the results of demetallation of the cycloaddition products by a number of methods. From these reactions it was clear that a particular requirement for the cycloaddition reaction was that the olefin must be electron deficient. It was considered that the use of an electron rich (η^1-allyl)-Fp complex [Fp = $Fe(CO)_2$(cyclopentadienyl)] might extend the scope of these processes. Dicarbonyl(η^5-cyclopentadienyl)(η^1-3-methoxyallyl)iron (2) has been prepared [2] and its reactions with a variety of electron-deficient olefins and acetylenes were studied.



(1) (2)

Fp = $Fe(CO)_2$(cyclopentadienyl)

RESULTS AND DISCUSSION

Reaction of (η^1-3-methoxyallyl)-Fp (2) with ethyl 3-3-dicyanoacrylate (3a) in dichloromethane at room temperature yielded a mixture of the two isomeric products (4a) and (5a) (Scheme 1), which were easily separated by column chromatography on Florisil, and were isolated in a 3 : 2 ratio, respectively.‡ Formation of four diastereoisomers was a possibility from this reaction, but earlier studies by Rosenblum *et al.*[3] have indicated that the geometrical relationship of Fp and the C-3 substituent in complex (2) is retained in the products. The structure (4a) (Scheme 1) was assigned to the major product as 2-H resonated as a doublet of doublets in the ^{1}H n.m.r. spectrum (Table 3), which indicated a β,β,α-configuration for 1-, 2-, and 3-H, respectively. However, 2-H resonated as a triplet in the spectrum of the minor product, indicating that 1-, 2-, and 3-H are β,β,β-, respectively, as in complex (5a).

TABLE 1

Reaction of (η^1-3-methoxyallyl)-Fp (2) with the electron-deficient olefins (3)

Olefin	Yield (%) of (4) + (5)	Ratio of (4) to (5)
(3a) [a]	85 [d]	3 : 2
(3b) [a]	89 [d]	2 : 3
(3c) + (3d) [a]	86	1 : 1
(3e) [b,c]	25 [e]	*f*
(3f) [b]	16 [e]	*f*

[a] Olefin (1 : 1 mol equiv.) and compound (2) in CH_2Cl_2 was stirred for 3 h. [b] Olefin (4 mol equiv.) and compound (2) in DMF was stirred for 90 h. [c] Dilute solution in DMF and compound (2). [d] Isolated by column chromatography on Florisil. [e] Isolated by column chromatography on Florisil and then neutral alumina (Act-III). [f] No compound (5) was formed.

Mixtures of the cyclic products (4b), and (5b) (4c) + (4d), and (5c) + (5d) were also obtained with diethyl 1-cyanoethylene-1,2-dicarboxylate (3b), ethyl 2,3-dicyanoacrylate (3c), and its isomer (3d), respectively. The ratio in which adducts were isolated depended upon the olefin employed (Table 1). Lower yields of the cyclopentanoid derivatives were obtained, even after longer reaction times, with diethyl methylenemalonate (3e) and trimethyl ethylenetricarboxylate (3f), probably due to the decreased reactivity of these olefins.

It is likely that the allyl complex would approach the olefin such that the methoxy- and R^3-substituents are in the more sterically favoured *trans*-configuration in the dipolar intermediate (7). Two processes could be postulated which would initially give this configuration [Scheme 2, (*a*) and (*b*)]. In the case of diethyl 1-cyanoethylene-1,2-dicarboxylate (3b), the considerable steric bulk of the ester groups would be expected to

† Part 1, preceding paper.

‡ The numbering given on the structures in this paper is that used to describe the n.m.r. spectral data and is not necessarily the numbering used in the IUPAC names.

TABLE 2

Physical and analytical data of the 2-methoxycyclopentyl-Fp complexes (4) and (5)

Product	Yield (%)	M.p. (°C)	Eluant ether : light petroleum	Formula	Required (%) C	H	N	Found (%) C	H	N
(4a)	49	89 [a]	1 : 1	$C_{18}H_{18}FeN_2O_5$	54.29	4.56	7.04	54.3	4.6	7.3
(5a)	36	140 [a]	3 : 1	$C_{18}H_{18}FeN_2O_5$	54.29	4.56	7.04	53.65	4.5	7.3
(4b)	33	99 [a]	2 : 3	$C_{20}H_{23}FeNO_7$	53.94	5.21	3.15	53.95	5.3	3.0
(5b)	56	103 [a]	3 : 2	$C_{20}H_{23}FeNO_7$	53.94	5.21	3.15	53.8	5.2	2.9
(4c) + (4d)	44	136 [a]	1 : 1—3.1	$C_{18}H_{18}FeN_2O_5$	54.29	4.56	7.04	54.1	4.75	6.9
(5c) + (5d)	42	163 [a]	*b*	$C_{18}H_{18}FeN_2O_5$	54.29	4.56	7.04	54.1	4.7	7.0
(4e)	25	65	1 : 3							
(4f)	16	125	3 : 1	$C_{19}H_{22}FeO_9$	50.69	4.93		50.65	5.2	

[a] Recrystallised from hexane–ether. [b] CH_2Cl_2 and acetone.

TABLE 3

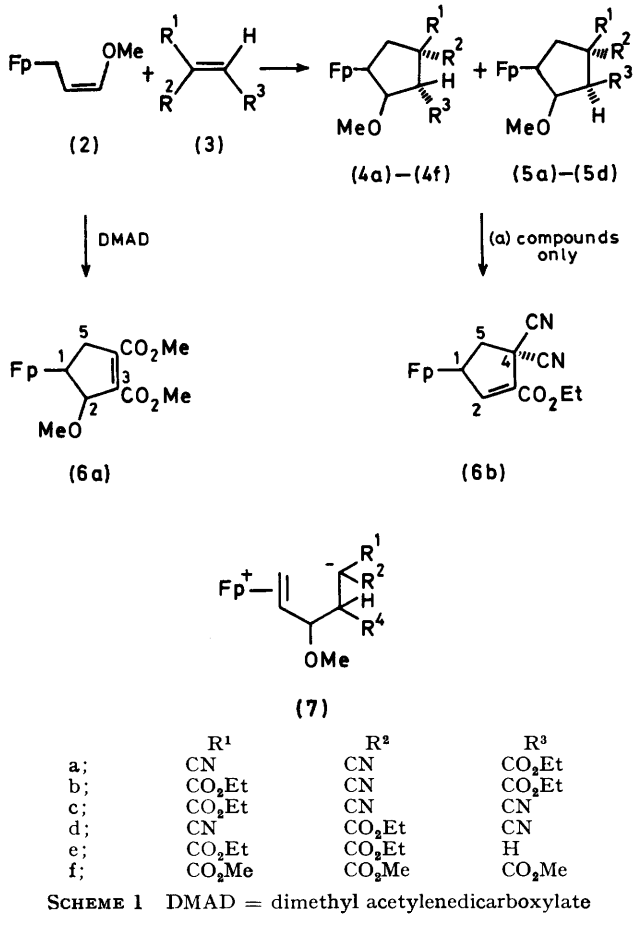
Spectral data of the Fp-complexes (4) and (5)

Product	$\nu_{max.}$/cm^{-1}	Spectral data: ^{1}H N.m.r. chemical-shift (δ, J in Hz)	Spectral data: *M/e* (% abundance) (at 25 eV)
(4a)	(in CH_2Cl_2) 2 240w (C≡N), 2 005, 1 960s (C≡O), 1 735s (C=O)	1.37 (3 H, t, CO_2CH_2*Me*), 2.30—3.02 (3 H, m, CH_2 and 1-H), 3.29 (3 H, s, OMe), 3.45 (1 H, d, J 2.5, 3-H), 3.95 (1 H, dd, J 5.5 and 2.5, 2-H), 4.32 and 4.35 (2 H, each q, 1 : 1 ratio, OCH_2), 4.83 (5 H, s, Cp)	398 (M^+, 0), 342 (27, (M^+ − 2CO), 246 (22), 219 (18), 152 (100), 149 (19), 122 (90), 121 (73)
(5a)	(in CH_2Cl_2) 2 242w (C≡N) 2 010, 1 960s (C≡O), 1 737s, (C=O)	1.36 (3 H, t, CO_2CH_2*Me*), 2.38—2.92 (3 H, m, CH_2 and 1-H), 3.34 (1 H, d, J 3.5, 3-H), 3.43 (3 H, s, OMe), 4.04 (1 H, t, J 3.5), 4.31 and 4.35 (2 H, each q, 1 : 1 ratio, OCH_2), 4.85 (5 H, s, Cp)	398 (M^+, 0), 342 (30, M^+ − 2CO), 246 (22), 219 (24), 152 (100), 149 (21), 122 (94), 121 (96), 91 (68)
(4b)	(in CH_2Cl_2) 2 010, 1 960s, (C≡O), 1 740s, (C=O)	1.30 and 1.35 (each 3 H, each t, CO_2CH_2*Me*), 2.10—2.50 (2 H, m, CH_2), 3.01 (1 H, ddd, J 12 and 6, 1-H), 3.18 (3 H, s, OMe), 3.71 (1 H, d, J 2.5, 3-H), 3.98 (1 H, dd, J 6 and 2.5, 2-H), 4.08—4.42 (4 H, m, OCH_2), 4.82 (5 H, s, Cp)	445 (M^+, 0), 389 (24, M^+ − 2CO) 324 (100, M^+ − 2CO, Cp), 294 (28), 122 (29), 121 (44), 93 (24), 92 (20), 40 (30)
(5b)	(in CH_2Cl_2) 2 010, 1 960s (C≡O), 1 740s (C=O)	1.30 and 1.34 (ecach 3 H, each t, CO_2CH_2*Me*), 2.35—2.84 (3 H, m, CH_2 and 1-H), 3.47 (3 H, s, OMe), 3.60 (1 H, d, J 3.5, 3-H), 4.02br (1 H, t, J 3.5, 2-H), 4.23 and 4.30 (each 2 H, each q, OCH_2), 4.82 (5 H, s, Cp)	445 (M^+, 0), 389 (21, M − 2CO), 325 (13), 324 (100), 294 (21), 293 (15), 121 (22)
(4c) + (4d)	(in $CHCl_3$) 2 242w (C≡N), 2 010, 1 970s (C≡O), 1 750s (C=O)	1.35 (3 H, t, CO_2CH_2*Me*), 2.12—3.09 (3 H, m, CH_2 and 1-H), 3.34 and 3.37 [3 H, each s, OMe of (4c) and (4d)] 3.75 (1 H, d, J 1.5, 3-H), 3.90 (1 H, dd, J 5.5 and 1.5, 2-H), 4.31 (2 H, q, OCH_2), 4.84 (5 H, s, Cp)	398 (M^+, 0.1) 342 (10, M^+ − 2CO), 246 (36), 152 (40), 149 (38), 122 (95), 121 (100), 117 (31)
(5c) + (5d)	(in $CHCl_3$) 2 242w (C≡N), 2 010, 1 967s (C≡O), 1 740s (C=O)	[in $(CD_3)_2CO$] 1.33 (3 H, t, CO_2CH_2*Me*), 2.18—2.82 (3 H, m, CH_2 and 1-H), 3.65 (3 H, s, OMe), 3.74 (1 H, d, J 3, 3-H), 4.07br (1 H, t, J 3, 2-H), 4.32 (2 H, q, OCH_2), 5.06 (5 H, s, Cp)	398 (M^+, 0), 342 (18, M − 2CO), 271 (32), 247 (30), 246 (57), 186 (40), 152 (47), 122 (61), 121 (100), 117 (51)
(4e)	(in $CHCl_3$) 2 010, 1 952s (C≡O), 1 722s (C=O)	1.23 (6 H, t, CO_2CH_2*Me*), 1.95—2.90 (5 H, m, 2 × CH_2 and 1-H), 3.20 (3 H, s, OMe), 3.57 (1 H, m, 2-H), 4.20 (4 H, q, OCH_2), 4.80 (5 H, s, Cp)	420 (M^+, 0), 3.64 (24, M^+ − 2CO), 300 (15), 299 (100, M − 2CO, Cp), 269 (31), 122 (17), 121 (37)
(4f)	(in $CHCl_3$) 2 005, 1 955s (C≡O), 1 735s (C=O)	2.20—2.90 (3 H, m, CH_2 and 1-H), 3.34 (3 H, s, OMe), 3.69 and 3.72 (each 3 H, each s, CO_2Me), 3.96 (2 H, m, 2-H and 3-H), 4.78 (5 H, s, Cp)	450 (M^+, 0), 394 (11, M − 2CO), 330 (15), 329 (100, M − 2CO, Cp), 299 (22), 151 (29), 121 (32), 71 (24), 65 (15), 59 (20)

favour the latter of these two processes [Scheme 2, (*b*)] resulting in the formation of complex (5b) in higher yield. By replacing one of the ester groups with a cyano-group, the steric hindrance may be reduced to such an extent that either the former process [Scheme 2, (*a*)] predominates, as with ethyl 3,3-dicyanoacrylate (3a), or that the olefin can approach the allyl complex equally from any direction, giving a 50 : 50 mixture, as with ethyl 2,3-dicyanoacrylate (3c) + (3d).

It was discovered that column chromatography on neutral alumina eliminated methanol from the adducts (4a) and (5a), yielding (6b) (Scheme 1). In general, complex (4a) was isolated in low yield (<15%) from the column, whereas complex (5a) always gave the product of elimination (6b), providing further evidence that these adducts have the stereochemistry shown since, even in a cyclopentyl derivative, a *trans-E*2 elimination reaction is probably more favoured. However, no elimination of methanol was apparent from the adducts (4b)—(4d) and (5b)—(5d) (Scheme 1).

Reaction of (η^1-3-methoxyallyl)-Fp (2) with dimethyl acetylenedicarboxylate (DMAD) has been found to be relatively slow when compared with the reactions with olefinic esters. Thus, reaction of complex (2) with DMAD (10 equiv.) in dimethylformamide (DMF) for 45 h at room temperature yielded 66% of the cyclic product (6a). This yield was, however, improved to 77% when the reaction was conducted with 4 equiv. of DMAD for a



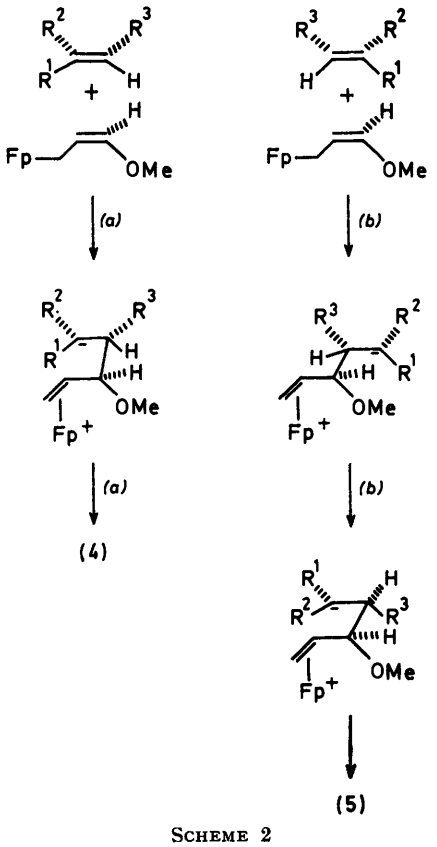
	R^1	R^2	R^3
a;	CN	CN	CO_2Et
b;	CO_2Et	CN	CO_2Et
c;	CO_2Et	CN	CN
d;	CN	CO_2Et	CN
e;	CO_2Et	CO_2Et	H
f;	CO_2Me	CO_2Me	CO_2Me

SCHEME 1 DMAD = dimethyl acetylenedicarboxylate

period of 48 h, followed by addition of another 2 equiv. and stirring for a further 24 h. Unlike in other cases, no improvement of yield of complex (6a) was obtained (51%) when the solvent was changed to dichloromethane. Isolation of the single cyclic product (6a) in a shorter time from the reaction of complex (2) with DMAD indicated its enhanced reactivity when compared with its simple allyl analogue (1), which yielded a mixture of linear and cyclic adducts. The absence of linear products from the former reaction might be due to the presence of the 3-methoxy-group in complex (2) which could disfavour abstraction of hydrogen from C-3 in the intermediate zwitterion (7).

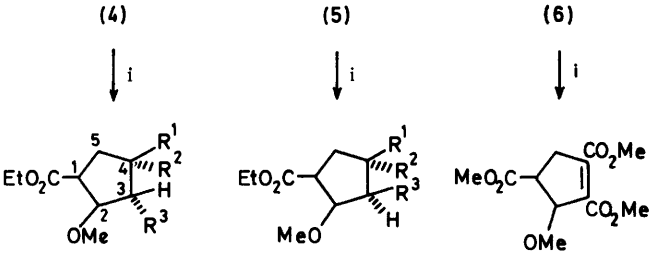
Demetallation Reactions.—For the cycloaddition reactions to be of synthetic use in organic chemistry, methods for the removal or replacement of the Fp-moiety in complexes (4), (5), and (6) by a suitable organic function are required. Demetallation reactions of these products have been studied under a variety of conditions.

(i) *Oxidative carboxylation.* The replacement of the Fp-group with a carboxylic ester function has been readily achieved by the oxidation of alcoholic solutions of alkyl-Fp complexes with cupric chloride,[9,10] ceric salts,[11,12] oxygen, or bromine.[10] Treatment of alcoholic solutions of the Fp-complexes (4a)—(4d), (5a)—(5d), and (6a) with ammonium ceric nitrate, in the presence of carbon monoxide, resulted in the corresponding carboxylated derivatives (8), (9), and (10) (Scheme 3, Table 4).



SCHEME 2

It was concluded that the oxidative carboxylation of complexes (4) and (5) proceeded with retention of configuration,[9] since only one methoxy-group resonance appeared in the ^1H n.m.r. spectra of the crude products.



	R^1	R^3	R^3
a;	CN	CN	CO_2Et
b;	CO_2Et	CN	CO_2Et
c;	CO_2Et	CN	CN
d;	CN	CO_2Et	CN

SCHEME 3 *Reagents* i, Ce^{IV}, ROH–CO

The derivatives (9a)—(9d), however, isomerised during chromatography to afford a mixture of isomers, as indicated by an increase in the number of methoxy-group

TABLE 4

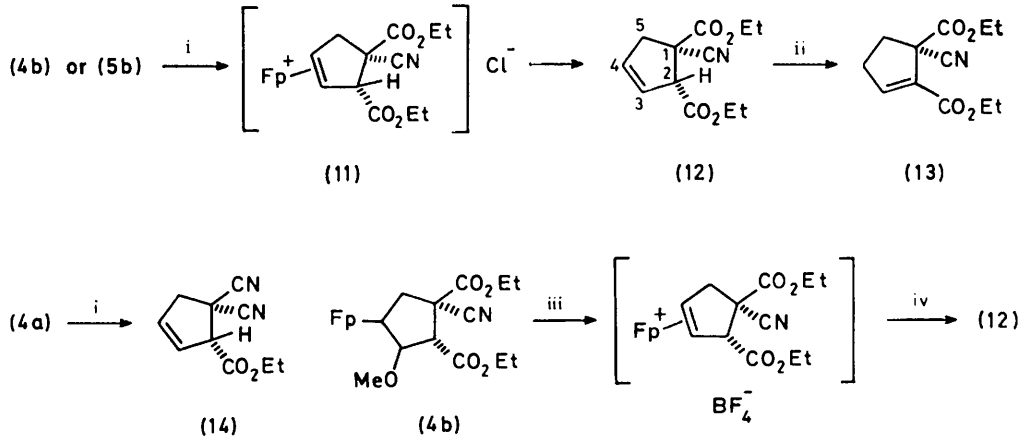
Carboxylation of the Fp-complexes (4), (5), and (6a)

Fp-adduct	Product [a]	Yield (%)	Spectral data: ^{1}H N.m.r. chemical shift (δ, J in Hz)	Spectral data: M/e (% abundance)
(4a)	(8a)	71 [b]	1.29 and 1.37 (each 3 H, each t, CO_2CH_2Me), 2.62—3.15 (2 H, m, CH_2), 3.30—3.56 (1 H, m, 1-H), 3.43 (3 H, s, OMe), 3.55 (1 H, d, J 4.5, 3-H), 4.06—4.32 (5 H, m, OCH_2 and 2-H)	294 (M^+, 1.0), 249 (20, (M^+ − OEt), 217 (28), 194 (36), 170 (51), 122 (33), 101 (100), 73 (53), 71 (30)
(5a)	(9a)	77 [b]	1.31 and 1.38 (each 3 H, each t, CO_2CH_2Me), 3.74 (1 H, dd, J 17.5 and 13.5, 5-H), 3.20—3.71 (3 H, m, 1-, 3-, and 5-H), 3.48 (3 H, s, OMe), 4.16 and 4.18 (each 2 H, each q, OCH_2), 4.58 (1 H, t, J 4, 2-H)	294 (M^+, 4), 249 (39, M^+ − OEt), 186 (45), 140 (100), 105 (40), 101 (74), 91 (42), 73 (54), 55 (52)
(4b)	(8b)	58 [b]	1.23—1.40 (9 H, m, CO_2CH_2Me), 2.50 (1 H, dd, J 6 and 3.5, 5-H), 2.82 (1 H, t, J 6, 5-H), 3.35—3.51 (1 H, m, 1-H), 3.39 (3 H, s, OMe), 3.71 (1 H, d, J 2.5, 3-H), 4.05—4.40 (6 H, m, OCH_2), 4.47 (1 H, dd, J 3.5 and 2.5, 2-H)	(at 25 eV) 341 (M^+, 0), 296 (31, M^+ − OEt), 241 (47), 195 (100), 170 (63), 167 (67), 140 (43), 105 (99)
(5b)	(9b) [d]	41 [c]	1.24—1.40 (9 H, m, CO_2CH_2Me), 2.21—2.6 (2 H, m, CH_2), 3.00—3.25 (1 H, m, 1-H), 3.50 (3 H, s, OMe), 3.64 (1 H, d, J 1.7, 3-H), 4.06—4.42 (6 H, m, OCH_2), 4.50 (1 H, m, 2-H); isomers 3.4 and 3.44 (each 3 H, each s, OMe), 3.72 (1 H, d, J 3, 3-H)	(at 25 eV) 341 (M^+, 6), 296 (42, M^+ − OEt), 195 (100), 167 (96), 149 (98), 140 (94), 103 (98), 71 (77), 57 (66), 43 (70)
(4c) + (4d)	(8c) + (8d)	75 [b]	1.27 and 1.37 (each 3 H, each t, CO_2CH_2Me), 2.71—2.80 (each 1 H, each dd, J 30.5 and 14, CH_2), 3.12—3.65 (1 H, m, 1-H), 3.48 and 3.50 [3 H, each s, *ca.* 4 : 1, OMe of (8c) and (8d)], 3.78 (1 H, d, J 6, 3-H), 4.06—4.52 (5 H, m, OCH_2 and 2-H)	294 (M^+, 0), 249 (26), 221 (19, M^+ − CO_2Et), 144 (100), 117 (20), 115 (23), 98 (33)
(5c) + (5d)	(9c) + (9d)	53 [c]	1.30 and 1.38 (each 3 H, each t, OCH_2Me), 2.48—2.98 (2 H, m, CH_2), 3.01—3.17 (1 H, m, 1-H), 3.54 (1 H, d, J 12, 3-H), 3.64 (3 H, s, OMe), 4.08—4.50 (5 H, m, OCH_2 and 2-H); isomers 3.48 (3 H, s, OMe), 3.79 (1 H, d, J 6, 3-H)	294 (M^+, 0), 249 (22), 221 (18), 175 (16), 144 (100), 115 (24), 113 (19), 98 (30), 71 (28)
(6a)	(10)	25	2.72 (1 H, dd, J 20 and 9.5, 5-H), 3.17—3.58 (2 H, m, 1- and 5-H), 3.45 (3 H, s, OMe), 3.77, 3.82, and 3.84 (each 3 H, each s, CO_2Me), 4.83 (1 H, dd, J 7 and 2.5, 2-H)	272 (M^+, 4), 240 (52, M^+ − MeOH), 210 (95), 165 (52), 153 (75), 75 (74), 59 (70)

[a] All the products indicated a strong peak at ν *ca.* 1 740 cm^{-1}; all these oily liquids were eluted from the column with ether–light petroleum (1 : 1). [b] Isolated yield. [c] Isolated as a mixture of isomers. [d] Ref. 1.

resonances in the ^{1}H n.m.r. spectra of the chromatographed products. This isomerisation of compounds (9a)—(9d) provides further evidence of an all *cis*-arrangement of substituents as shown in structure (9), which would be expected to rearrange on the column to the structure with the more stable configuration. The low isolated yield of compound (10) (25%) is considered to be due to decomposition during chromatography, as the ^{1}H n.m.r. spectrum of the crude product indicated its quantitative formation.

(ii) *Acid cleavage.* In contrast with the oxidative cleavage of the Fp-moiety, very few acid cleavages have been investigated.[13,14] Treatment of a dichloromethane solution of the cyclopentyl-Fp complexes (4b) or (5b) with hydrogen chloride for 1 h resulted in exclusive formation of compound (12) in yields of 75—81%. The i.r. spectrum of the crude reaction mixture indicated that the reaction proceeded *via* the Fp-(η^1-olefin) cation (11) (Scheme 4). Similar observations were made earlier [15] in the treatment of a 2-methoxyethyl-Fp complex with hydrogen chloride, which resulted in the formation of a Fp-(η-ethylene) cation. Treatment of an ethanolic solution of compound (12) with sodium ethoxide gave compound (13), in which the olefinic proton resonated



SCHEME 4 Reagents: i, HCl, CH_2Cl_2, 0 °C; ii, NaOEt, iii, Ph_3CBF_4; iv, NaI, AcMe

as a triplet (δ 7.15, *J* 2 Hz). The adduct (4a) also gave the eliminated product (14) in 56% yield on reaction with HCl (Scheme 4).

(iii) *β-Hydride abstraction.* Conversion of alkyl-Fp complexes into Fp-(η-olefin) cations followed by treatment with sodium iodide with liberation of an alkene has been developed previously [12,16,17] as a method for replacement of the Fp-group. Treatment of the Fp-complex (4b) with trityl tetrafluoroborate followed by reaction of the intermediate Fp-(η¹-olefin)-tetrafluoroborate salt (15) (Scheme 4) with sodium iodide in acetone gave compound (12) as the exclusive product in 62% yield.

The presence of the 2-methoxy-group in the cyclopentyl-Fp complexes (4) and (5) facilitates the easy cleavage of the Fp-moiety with hydrogen chloride and trityl tetrafluoroborate, resulting in formation of the cyclopentene derivatives (12) and (14). This is in contrast with the simple cyclopentyl-Fp adducts derived from (η¹-allyl)-Fp (1) which, with HCl, yielded a mixture of cyclic and linear products [8] by opening of the cyclopentane ring. This might be due to the greater ease of formation of the Fp-(η²-olefin) salt (11) by the elimination of the 2-methoxy-group, preceded by protonation.

EXPERIMENTAL

All operations were performed as described previously.[8] Dicarbonyl(η⁵-cyclopentadienyl)(η¹-3-methoxyallyl)iron (2) was prepared following the procedure of Rosenblum *et al.*[2] and used in the reactions. Fp = dicarbonyl(η⁵-cyclopentadienyl)iron, Cp = cyclopentadienyl, ether refers to diethyl ether, and ν is given in cm^{-1}.

Reactions of Complex (2) *with the Electron-deficient Olefins* (3a)—(3f).—*General procedure.* To a solution of the allyl complex (2) (*ca.* 2 mmol) in either dimethylformamide (DMF) or CH_2Cl_2 (5—15 ml) (Table 1) was added the olefin (3) (1—10 equiv.) dissolved in the same solvent (1—5 ml). The mixture was stirred at room temperature (Table 1). After removal of the solvent under reduced pressure (DMF at 0.1 Torr and CH_2Cl_2 at 14 Torr) the crude product was chromatographed with a 20 mm × 30 cm column. The residue was, in general, applied to the column as a solution in benzene (2—5 ml), the solvent being removed on elution with light petroleum followed by elution with ether–light petroleum (Table 2).

All the products * showed satisfactory spectral (Table 3) and analytical data (Table 2).

Elimination of Methanol from Complexes (4a) *and* (5a).—Reaction of the 3-methoxyallyl complex (2) (645 mg, 2.6 mmol) with ethyl 3,3-dicyanoacrylate (3a) (412 mg, 2.7 mmol) was carried out in dichloromethane (20 ml) employing the standard reaction procedure. Column chromatography of the crude product, obtained after removal of the solvent under reduced pressure, on neutral alumina (Act-III) afforded the cyclic adduct (4a) [153 mg, 13%, ether–light petroleum (1 : 1) as eluant] and dicarbonyl(η⁵-cyclopentadienyl)(η¹-4,4-dicyano-3-ethoxycarbonylcyclopent-2-enyl)-iron (6b), eluted by ether (Scheme 1, 287 mg, 32%); $\nu_{max.}$ (CH_2Cl_2) 2 242w (C≡N), 2 010, 1 970s (C≡O), 1 700s (C=O), and 1 595m (C=C); δ 1.37 (3 H, t, CO_2CH_2Me), 2.64br (1 H, dd, 5-H), 3.12—3.4 (1 H, m, 5-H), 3.56 (1 H, m, 1-H), 4.34br (2 H, q, OCH_2), 4.9 (5 H, s, Cp), and 7.39br (1 H, d, *J* 2.5 Hz, 2-H).

Reaction of Complex (2) *with Dimethyl Acetylenedicarboxylate (DMAD).*—DMAD (0.8 ml, *ca.* 6 mmol) was added in one portion to a solution of the allyl complex (2) (367 mg, 1.5 mmol) in DMF (10 ml). After the mixture had been stirred for 48 h, an additional 2 equiv. of DMAD (0.4 ml, *ca.* 3 mmol) was added, and the reaction was continued for 24 h. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina (Act-III). *Dicarbonyl(η⁵-cyclopentadienyl)(η¹-2-methoxy-3,4-dimethoxycarbonylcyclopent-3-enyl)iron* (6a) (446 mg, 77%) was eluted with ether–light petroleum (1 : 1), and recrystallised from a mixture of hexane–ether to obtain a yellow solid, m.p. 94—96 °C (Found: C, 52.4; H, 4.7. $C_{17}H_{18}FeO_7$ requires C, 52.33; H, 4.65%); $\nu_{max.}$ ($CHCl_3$) 2 000, 1 955s (C≡O), 1 715s (CO_2Me), and 1 632m (C=C); δ 2.58—3.10 (3 H, m, CH_2 and 1-H), 3.38 (3 H, s, OMe), 3.79 and 3.81 (each 3 H, s, CO_2Me), 4.26br (1 H, dd, *J ca.* 4 and 1.5 Hz, 2-H), and 4.85 (5 H, s, Cp); *m/e* 390 (M^+, 0%), 237 (55), 122 (43), 121 (54), 119 (100), 95 (35), 92 (29), and 77 (25).

Oxidative Carboxylation of the Fp-adducts (4), (5), *and* (6a).—*General procedure.* To a solution of the Fp-complex [(4), (5), and (6a)] in either anhydrous methanol or ethanol (40 ml), previously purged with carbon monoxide for 2 h, was added ammonium ceric nitrate (4 equiv.) in one portion at room temperature. Carbon monoxide was then bubbled through the solution overnight. After removal of the solvent under reduced pressure, water (50 ml) was added to the solid residue and the aqueous solution was extracted with benzene (4 × 25 ml). The combined organic extracts were dried (anhydrous Na_2SO_4), after which the solution was filtered, concentrated, and the crude product chromatographed on Florisil with ether–light petroleum as eluant. All the products † showed satisfactory spectral data (Table 4).

Acid Cleavage of the Fp-complexes (4a), (4b), *and* (5b).—*General procedure.* Hydrogen chloride gas was bubbled through a solution of the Fp-adducts (*ca.* 0.4 mmol) in dichloromethane (*ca.* 40 ml) at 0 °C for 1 h, and the reaction mixture was then set aside for *ca.* 20—24 h. After removal of the solvent under reduced pressure, the residue was

* *Dicarbonyl(η⁵-cyclopentadienyl)(η¹-4,4-dicyano-t-3-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (4a), *dicarbonyl(η¹-t-4-cyano-t-3,c-4-diethoxycarbonyl-r-2-methoxycyclopentyl)(η⁵-cyclopentadienyl)iron* (4b), *dicarbonyl(η⁵-cyclopentadienyl)(η¹-t-3,t-4-dicyano-c-4-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (4c), *dicarbonyl(η⁵-cyclopentadienyl)(η¹-c-3,c-4-dicyano-t-4-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (4d), *dicarbonyl(η⁵-cyclopentadienyl)(η¹-4,4-diethoxycarbonyl-2-methoxycyclopentyl)iron* (4e), *dicarbonyl(η⁵-cyclopentadienyl)(η¹-r-2-methoxy-c-3,4,4-trimethoxycarbonylcyclopentyl)iron* (4f), *dicarbonyl(η⁵-cyclopentadienyl)-(η¹-4,4-dicyano-c-3-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (5a), *dicarbonyl(η¹-t-4-cyano-c-3,c-4-diethoxycarbonyl-r-2-methoxycyclopentyl)(η⁵-cyclopentadienyl)iron* (5b), *dicarbonyl(η⁵-cyclopentadienyl)(η¹-c-3,t-4-dicyano-c-4-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (5c), and *dicarbonyl(η⁵-cyclopentadienyl)-(η¹-t-3,c-4-dicyano-t-4-ethoxycarbonyl-r-2-methoxycyclopentyl)iron* (5d)

† Diethyl 4,4-dicyano-*c*-2-methoxycyclopentane-*r*-1,*t*-3-dicarboxylate (8a), triethyl 1-cyano-*c*-3-methoxycyclopentane-*r*-1,*t*-2,*c*-4-tricarboxylate (8b), diethyl 1,*t*-5-dicyano-*c*-4-methoxycyclopentane-*r*-1,3-*c*-dicarboxylate (8c), diethyl 1,*c*-5-dicyano-*t*-4-methoxycyclopentane-*r*-1,3-*t*-dicarboxylate (8d), diethyl 4,4-dicyano-*c*-2-methoxycyclopentane-*r*-1,*c*-3-dicarboxylate (9a), triethyl 1-cyano-*c*-3-methoxycyclopentane-*r*-1,*c*-2,*c*-4-tricarboxylate (9b), diethyl 1,*c*-5-dicyano-*c*-4-methoxycyclopentane-*r*-1,*c*-3-dicarboxylate (9c), diethyl 1,*t*-5-dicyano-*t*-4-methoxycyclopentane-*r*-1,*t*-3-dicarboxylate (9d), and trimethyl 3-methoxycyclopent-1-ene-1,2,4-tricarboxylate (10).

dissolved in carbon tetrachloride (*ca.* 50 ml) and exposed to sunlight for 3 h to decompose any FpCl present, during which time a green solid precipitated. This solid was then filtered off, the filtrate concentrated, and the crude product purified by flash chromatography [18] [silica gel (10 g), 20 mm column]. The yields and spectral data are as given below.

(i) *Acid cleavage of complex* (4a). When complex (4a) was treated with HCl as described in the above procedure, ethyl 5,5-dicyanocyclopent-2-ene-1-carboxylate (14) was isolated (56%) by elution with a mixture of ether–light petroleum (1 : 1) from the column; $\nu_{max.}$ (CH_2Cl_2) 1 742s (C=O); δ 1.31 and 1.36 (3 H each t, 3 : 4 ratio, CO_2CH_2Me), 3.10 and 3.30 (2 H, m, 3 : 4 ratio, CH_2), 3.91 (1 H, s, $CHCO_2$-Et), 4.12—4.33 (2 H, m, OCH_2), 6.87 and 6.97br (2-H, s, 3 : 4 ratio, CH=CH); *m/e* 190 (M^+, 0.1%), 124 (27), 117 (22), 106 (14), 92 (24), 91 (100), and 71 (14).

(ii) *Acid cleavage of complexes* (4b) *and* (5b). Similar treatment of complexes (4b) or (5b) with HCl yielded diethyl 1-cyanocyclopent-3-ene-1,2-dicarboxylate (12) (yield 81%), eluted by 20% ether in light petroleum; $\nu_{max.}$ 1 740s (C=O, ester); δ 1.31 and 1.37 (each 3 H, t, CO_2-CH_2Me), 3.10 (2 H, dd, *J* 3.5 and 1.5 Hz, CH_2), 4.10—4.40 (5 H, m, OCH_2 and $CHCO_2Et$), and 5.90br (2 H, s, CH=CH); *m/e* (25 eV) 237 (M^+, 5%), 191 (38), 163 (24), 138 (32), 118 (23), 93 (23), 92 (100), 91 (65), and 65 (22). Compound (12b) was obtained from complex (5b) in 75% yield.

Isomerisation of the Dicarboxylate (12) *to the Dicarboxylate* (13).—To a solution of compound (12) (155 mg, 0.65 mmol) in anhydrous ethanol (1 ml) was added sodium ethoxide [prepared from sodium (15 mg, 0.65 mmol)] dissolved in ethanol (1 ml). After being stirred at room temperature for 30 s, the reaction mixture was neutralised with 0.1N hydrochloric acid and then partitioned between dichloromethane (10 ml) and saturated aqueous sodium chloride (10 ml). The organic layer was separated and the aqueous phase further extracted with dichloromethane (4 × 10 ml) and the combined extracts were dried (anhydrous $MgSO_4$), and concentrated. Flash chromatography,[18] [silica gel (10 g), 20 mm column] with ether–light petroleum (1 : 1) as eluant, afforded pure diethyl 1-cyanocyclopent-2-ene-1,2-dicarboxylate (13) as an oily liquid (121 mg, 78%); $\nu_{max.}$ (CH_2Cl_2) 1 720—1 745s (CO, ester); δ 1.32 and 1.35 (each 3 H, each t, CO_2CH_2Me), 2.44—2.40 (4 H, m, 2 × CH_2), 4.29 and 4.31 (each 2 H, each q, OCH_2), and 7.15br (1 H, t, *J* 2 Hz, H_2CCH=C); *m/e* (25 eV) 237 (M^+, 10%), 192 (10), 165 (28), 164 (17), 137 (56), 120 (13), 119 (100), 92 (33), and 91 (24).

The yield of the isomerised product (13) decreased to 38% when the reaction mixture was stirred for 5 min.

Reaction of the Fp-complex (4b) *with Trityl Tetrafluoroborate*.—A solution of trityl tetrafluoroborate (90 mg, 0.27 mmol) in dichloromethane (2 ml) was added as drops to a solution of complex (4b) (119 mg, 0.27 mmol) in the same solvent (3 ml) at 45 °C. The reaction was completed by stirring this mixture for 2 h at 45 °C (monitored by i.r. spectroscopy); the reaction mixture was then cooled to 0 °C and the intermediate Fp-(η^2-olefin) salt (15) (Scheme 3) was precipitated by adding ether (*ca.* 30 ml). The solvent was decanted off and the residue washed with ether (*ca.* 20 ml) to give the salt (15) (112 mg, 76%) (Scheme 3); $\nu_{max.}$ (CH_2Cl_2) 2 075 and 2 030s (C≡O).

To the above salt dissolved in acetone (2 ml) was added sodium iodide (63 mg, 0.42 mmol) in one portion and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (*ca.* 10 ml). The extracts were filtered (to remove the excess of sodium iodide) and concentrated. The crude product was then dissolved in carbon tetrachloride (20 ml). The solution was exposed to sunlight for 3 h (to decompose any FpI present), filtered, and the solvent removed under reduced pressure. Flash chromatography [silica gel (10g), 20 mm column], with ether–light petroleum (1 : 4) as eluant, afforded the dicarboxylate (12) [39 mg, 62% from (4b)].

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