Metal-assisted Cycloadditions. Part 1. Synthesis of Substituted Cyclopentane-derivatives obtained from the Reactions of (η^1-Allyl)dicarbonyl-(η^5-cyclopentadienyl)iron with Electron-deficient Olefins and Acetylenes

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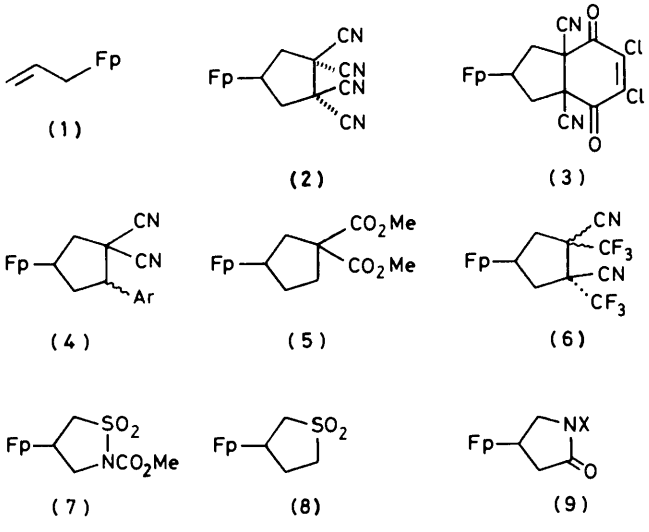
(η^1-Allyl)dicarbonyl(η^5-cyclopentadienyl)iron has been treated with various electron-deficient cyano- and alkoxycarbonyl-substituted olefins and dimethyl acetylenedicarboxylate. The resulting cyclopentyl–Fp [Fp = $Fe(CO)_2$(cyclopentadienyl)] complexes have been subjected to demetallation reactions employing various reagents. Alkoxycarbonyl esters of the substituted cyclopentanes were isolated by oxidative carboxylation with ceric ammonium nitrate, and cyclic and linear products have been obtained with hydrogen chloride by cleavage of the Fe–C bond. *N*-Bromopyridinium bromide has yielded a mixture of bromocyclopentane derivatives and cyclopentenes. β-Hydride abstraction, with trityl tetrafluoroborate, of the complex (12c) has resulted in the formation of diethyl but-3-enylmalonate.

THE reaction of (η^1-allyl)dicarbonyl(η^5-cyclopentadienyl)iron(1) † with tetracyanoethylene has been reported [1] to yield the cycloaddition product (2) and this reaction has been applied to the synthesis of a number of cyclopentanoid derivatives of complex (2).[2-5] A variety of other electrophilic, unsaturated moieties have been shown to undergo a similar cycloaddition reaction with complex (1). Reactions with dichlorodicyano-*p*-quinone,[1] *o*-chloro-β,β-dicyanostyrene, dimethyl methylenemalonate,[3] 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene,[5] *N*-sulphonylurethane,[3] and sulphene [3] gave the



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

adducts (3)—(8). Similarly, reaction with isocyanates yielded adducts of the general structure (9).

These reactions are considered to proceed *via* a two-step process involving initial formation of a dipolar ion [*e.g.* (13), Scheme 2) followed by cyclisation.[1,4] Evidence for this has been provided by the characterisation of a dipolar metal–olefin complex in the reaction of complex (1) with sulphur dioxide [6] and by the dependence of the rate of reaction of these cycloaddition reactions on the polarity of the solvent employed.[4] Further evidence for a dipolar intermediate is provided by a number of processes which have been observed to compete with closure of the zwitterion. These include proton transfer, insertion,[7] and intramolecular zwitterion decomposition.[8] Whilst the overall process apparently proceeds in two stages, the stereochemistry of the cycloaddition reactions has been shown [3] to correspond to a suprafacial addition of the electrophile to the allyl complex. The geometric relationship associated with a substituent at C-3 and the Fp-moiety [Fp = $Fe(CO)_2$(cyclopentadienyl)] in the (η^1-allyl)-Fp complex (1) is preserved in the product.[3]

We report herein a detailed study of the reaction of complex (1) with a number of cyano- and alkoxycarbonyl-substituted olefins (11) in an attempt to define the degree of reactivity in the Fp-complex. Studies on the demetallation of the cycloaddition product with formation of cyclopentanoid derivatives are also reported. In subsequent papers we compare the reactivity of complex (1) with analogous complexes containing 2- and 3-methoxy-groups.[9]

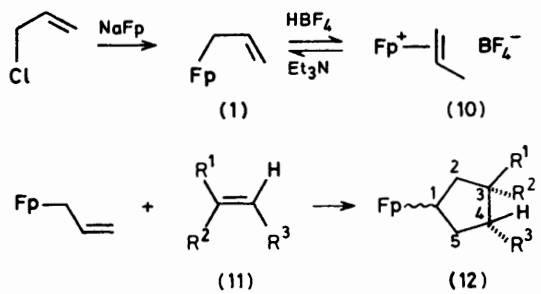
RESULTS AND DISCUSSION

The (η^1-allyl)dicarbonyl(η^5-cyclopentadienyl)iron complex (1) was prepared by a slight modification of the procedure described earlier.[10] Allyl chloride was treated with NaFp and the product was treated with fluoroboric acid to give the tetrafluoroborate salt (10) in an overall yield of 86%. This allyl complex was regenerated quantitatively from the salt (10) by treatment with triethylamine.

Reaction of complex (1) with the dicarboxylate ‡ (11a), (Scheme 1) in dichloromethane for 1 h led to isolation of the crystalline Fp-complex (12a) in *ca.* 80% yield. As expected, the formation of a mixture of diastereoisomers was indicated by the presence of two cyclopentadienyl

† 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.

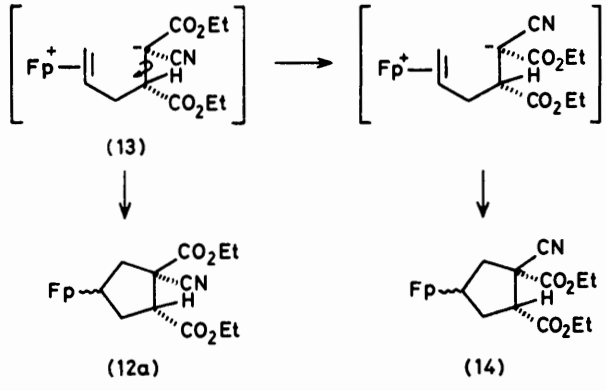
‡ The dicarboxylate (11a) was prepared by the procedure used for its dimethyl analogue, H. K. Hall, jun., and P. Ykman, *J. Am. Chem. Soc.*, 1975, **97**, 800.



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

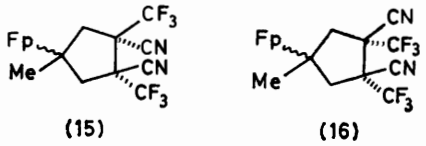
SCHEME 1

resonances and several quartets for OCH_2 of the ester groups in the H^1 n.m.r. spectrum of complex (12a). It is feasible that bond rotation about the indicated carbon bond of the dipolar intermediate (13) in the above reaction may lead to the formation of the cyclic adduct (14) as well as the complex (12a) (Scheme 2). Williams



SCHEME 2

and Wojcicki [5] have shown, however, that the thermodynamically more stable *trans*-configuration of 1,2-bis(trifluoromethyl)ethylene is retained in the cyclic product (15), whereas the *cis*-olefin isomerises during the reaction by bond rotation, to afford a mixture of complexes (15) and (16) in a 3 : 1 ratio. Thus, it is probable that complex (12a) is the predominant product in the



reaction of the Fp-complex (1) and the dicarboxylate (11a).

The cyclic adducts (12b)—(12g) (in good yields) were also obtained by reaction of complex (1) with dimethyl methylenemalonate (11g),[11] diethyl methylenemalonate (11b), trimethyl ethylenetricarboxylate (11c),[12] ethyl 3,3-dicyanoacrylate (11d), ethyl 2,3-dicyanoacrylate (11e),[13,14] and its isomer (11f).* The yields of the reactions together with the reaction conditions employed are summarised in Table 1. The cyclic adducts (12) were, in general, air stable and crystalline and existed as a mixture of diastereoisomers, which is indicated by two cyclopentadienyl resonances and several OMe singlets or OCH_2-quartets in the ^1H n.m.r. spectra (Table 2).

It could be anticipated that the choice of solvent would be important, as the intermediate zwitterion (13) would be stabilized by polar solvents if the reactions proceeded as shown in Scheme 2. No products were isolated from the reaction of complex (1) with trimethyl ethylenetricarboxylate (11c) in dichloromethane or tetrahydrofuran (THF) (Table 1). However, a good yield of the cyclic adduct was obtained in dimethylformamide (DMF).

Reaction of Complex (1) *with Acetylenes.*—Reaction of complex (1) with dimethyl acetylenedicarboxylate (DMAD) (2 equiv.) in DMF at room temperature for 90 h resulted in the formation of three 1 : 1 addition products in a ratio of 17 : 5 : 78, isolated in an overall yield of 54% by column chromatography over neutral alumina.

The collapse of the dipolar intermediate zwitterion (17) (Scheme 3) could follow several routes: (*a*) cyclisation, (*b*) H-transfer, and (*c*) insertion. The latter two processes would give rise to linear products. A similar type of insertion reaction has been reported earlier.[15,16] Examination of the ^1H n.m.r. spectrum indicates that

* Used as a mixture of *cis*- and *trans*- isomers (8 : 1).

TABLE 1

Formation of cyclopentyl-Fp complexes (12) from the reaction of the complex (1) and the electron-deficient olefins (11)

Olefin (11)	Amount of olefin (mol equiv.)	Solvent	Reaction time (h)	Recovered starting material (%)	Yield of the product [a] (12) (%)
a	1.1	DMF	1		69 [b]
	1.1	CH_2Cl_2	1		81
b	2	CH_2Cl_2	20		70 [c]
c	3	DMF	90		50 [c]
	2.5	DMF	70	50	24
	2	CH_2Cl_2	70	53	
	2	C_6H_6	70	58	
d	1.1	CH_2Cl_2	1		67 [c]
e + f	1.1	CH_2Cl_2	1		83 [d,e]
	1.25	CH_2Cl_2	1		94 [f]
g	2	CH_2Cl_2	20		64 [c]

[a] Isolated yields from column chromatography on neutral alumina (Act-III). [b] Ether–light petroleum (1.1—3 : 1) as eluant. Ether–light petroleum (1 : 1) as eluant. [d] From florisil column. [e] Ether–light petroleum (3 : 1) as eluant.

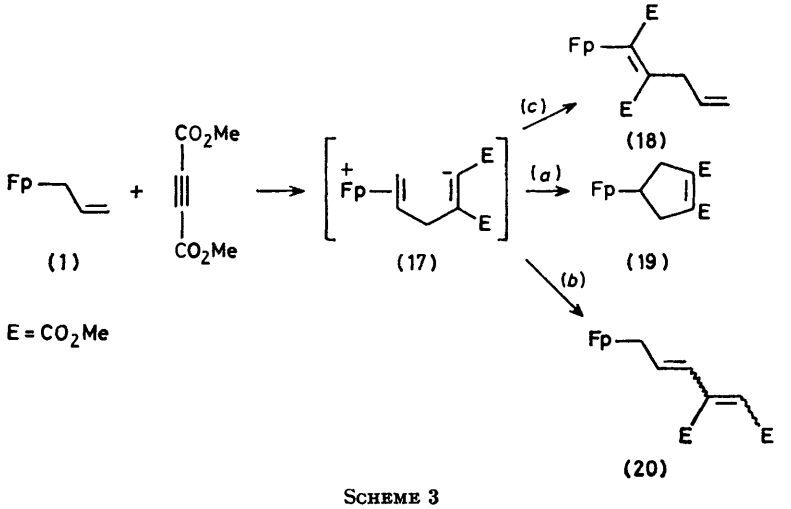
TABLE 2
Spectral and analytical data of the cyclopentyl–Fp adducts (12)

Product	M.p. (°C)	Spectral data: $\nu_{max.}$/cm^{-1}	Spectral data: ^{1}H N.m.r. chemical shift (δ, J in Hz)	Spectral data: *M/e* [a] (at 25 eV)	Formula	Analysis (%) Found (required): C	H	N
(12a) [b]		(in CH_2Cl_2) 2 245w (C≡N), 2 010, 1 952s (C≡O), 1 740s (C=O)	1.29 and 1.36 (each 3 H, t, CO_2CH_2Me), 1.78—3.06 (5 H, m, 2 × CH_2 and 1-H), 3.18—3.56 (0.5 H, m, 4-H), 3.86 (0.5 H, dd, *J* 11 and 7.5, 4-H), 4.23 and 4.30 (each 2 H, each q, OCH_2), 4.83 and 4.86 (5 H, each s, 1 : 1 ratio, Cp)	415 (*M*$^+$, 0), 359 (19), 293 (57), 221 (23), 149 (24), 148 (20), 121 (100), 93 (27), 92 (21)				
(12b)	70 [c]	(in $CHCl_3$) 2 000, 1 945s, (C≡O), 1 720s (C=O)	1.24 (6 H, t, CO_2CH_2Me), 1.73—2.78 (7 H, m, 3 × CH_2 and 1-H), 4.18 (4 H, q, OCH_2), 4.80 (5 H, s, Cp)	390 (*M*$^+$, 0), 334 (44), 293 (48), 122 (36), 121 (100), 95 (43), 67 (70), 66 (37)	$C_{18}H_{22}FeO_6$	55.15 (55.40)	5.85 (5.65)	
(12c)	105 [c]	(in $CHCl_3$) 2 000, 1 950s (C≡O), 1 730s (C=O)	1.60—3.06 (5 H, m, 2 × CH_2 and 1-H), 3.67, 3.70, 3.75, and 3.97 (9 H, each s, CO_2Me), *ca.* 3.70 (1 H, m, 4-H), 4.83 (5 H, s, Cp)	420 (*M*$^+$, 0), 364 (53), 270 (100), 212 (35), 151 (39), 121 (80), 93 (39), 65 (40)	$C_{18}H_{20}FeO_8$	51.3 (51.45)	4.6 (4.80)	
(12d)	88 [c]	(in $CHCl_3$) 2 248w (C≡N) 2 008, 1 955 (C≡O), 1 737s (C=O)	1.32, 1.33, and 1.35 (3 H, each t, CO_2CH_2Me), 1.76—2.95 (5 H, m, 2 × CH_2 and 1-H), 3.32 (0.3 H, dd, *J ca.* 11 and 7, 4-H), 3.41 (0.7 *H*, dd, *J* 12 and 6-, 4-H), 4.24, 4.25, and 4.28 (2 H, each q, OCH_2), 4.88 (5 H, s, Cp)	368 (*M*$^+$, 0), 312 (81), 285 (52), 270 (48), 246 (82), 219 (100), 149 (34), 147 (40), 121 (68)	$C_{17}H_{16}FeN_2O_4$	55.15 (55.46)	4.4 (4.38)	7.6 (7.61)
(12e) + (12f) [e]	116 [d]	(in $CHCl_3$) 2 240w (C≡N), 2 000, 1 955s, (C≡O), 1 740s, C=O)	1.36 (3 H, t, CO_2CH_2Me), 1.75—3.00 (5 H, m, 2 × CH_2 and 1-H), 3.43br (0.25 H, dd, *J ca.* 9.5 and 6-, 4-H), 3.61 (0.75 H, dd, *J* 10 and 5.5, 4-H), 4.33 (2 H, q, OCH_2), 4.83 and 4.89 (5 H, each s, 5 : 1 ratio, Cp)	368 (*M*$^+$, 0), 312 (10), 246 (23), 121 (100), 93 (43), 92 (31), 66 (38), 65 (42)	$C_{17}H_{16}FeN_2O_4$	55.3 (55.46)	4.55 (4.36)	7.45 (7.61)

[a] %-Abundance given in parentheses. [b] Compound (12a) is an amber oil. [c] Recrystallised from hexane–ether. [d] Recrystallised from ether. [e] Ref. 3.

the product obtained in 9% yield is the insertion product (18), since the spectrum contained a doublet at δ 3.09, corresponding to a CH_2-group, as well as peaks due to the three olefinic protons. The major and minor products showed spectral characteristics of the cyclic and H-transfer adducts, respectively, and hence were assigned the structures (19) and (20), respectively.

The reaction of complex (1) with DMAD is different to that of the (2- and 3-methoxyallyl)-Fp complexes with the same acetylene derivative. With these latter two complexes exclusively linear and cyclic products were obtained,[9] respectively. The formation of three products with simple Fp-allyl (1) might indicate a lower reactivity towards DMAD. Only starting material



SCHEME 3

was recovered from the reaction of complex (1) with 4 equiv. of methyl propiolate in DMF at room temperature for 80 h.

Demetallation Studies.—After preparation of the cyclopentyl-Fp complexes in a single step by cycloaddition reactions, the initial objective was to study the replacement of the Fp-group with a suitable functionality so that the resulting cyclopentane derivatives could be conveniently used in organic syntheses. Several procedures have been used for this purpose: (i) oxidative carboxylation, (ii) acid cleavage, (iii) bromination, and (iv) β-hydride abstraction.

(i) *Oxidative carboxylation.* Alcoholic solutions of the alkyl-Fp complexes have been converted into the corresponding alkyl esters with ceric salts,[17,18] oxygen,[16] bromine,[16] or cupric chloride.[19,20] An alcoholic solution of the cyclopentyl-Fp complex [(12a)—(12f) and (19)] was treated with ceric ammonium nitrate in an atmosphere of carbon monoxide and yielded the corresponding alkoxycarbonyl esters (21a)—(21f) and (22) (Scheme 4) in good yields (Table 3). Once again, from the n.m.r. data (Table 3) of the products (21a)—(21f), it can be concluded that these products were obtained as a mixture of isomers.

These reactions probably proceed by a three-step process, *via* the oxidised form of the iron complex (23). Ligand transfer (alkyl group to the carbonyl) within such a species is greatly facilitated by the increased electron deficiency at the carbonyl carbon atom due to the diminished back-bonding from the metal. Subsequent nucleophilic displacement of the rearranged cation (24), which again is likely to be facilitated by the positive charge on the iron, would result in the formation of the esterified products.

(ii) *Acid cleavage.* Hydrogen chloride has previously been used [21] to replace the Fp-moiety with hydrogen and this reaction has been found to proceed with a high degree of stereospecificity.[22] Generally, the reaction involved bubbling HCl gas into the dichloromethane solution of the cyclopentyl-Fp complex (12) at 0 °C for 1 h. A single product was isolated (67% yield) from the reaction of the Fp-complex (12b) with HCl, which was characterised as the malonate (25b) from its spectral data and by comparing it with an authentic sample prepared [23] by the reaction of sodium salt of diethyl malonate with 4-bromobutene (Scheme 5). The reaction clearly proceeded *via* the cationic intermediate (26), since the i.r. spectrum of the crude reaction mixture contained carbon monoxide stretching frequencies ($\nu_{max.}$ 2 075 and 2 040 cm^{-1}), characteristic of Fp-(η^2-olefin) salts.[18]

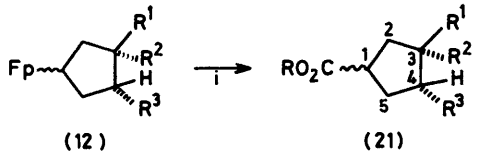
In addition to the analogous linear products (25a) and (25c) obtained from the reaction of the corresponding cyclopentyl-Fp adducts (12a) and (12c) with HCl, formation of the cyclopentane derivatives (27a) and (27c) was also observed, as a result of Fe–C cleavage in the ratios of 1 : 2 [(25a) : (27a)] and 1 : 1 [(25c) : (27c)], respectively (Table 4). The formation of the cyclic products in these two cases may be due to the presence of the electron-withdrawing group R^3, which causes a reduction in the electron density on the ester carbonyl at C-3 (to which R^1 and R^2 are attached), thus inhibiting

TABLE 3

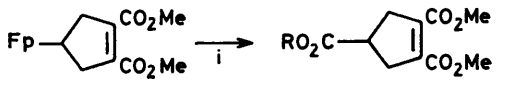
Oxidative carboxylation of the cyclopentyl-Fp complexes (12a)—(12f) and (19)

Fp-adduct	Product [a]	Yield [b] (%)	Solvent	Spectral data: ^{1}H N.m.r. chemical shift, (δ, *J* in Hz)	Spectral data: *M/e* (% abundance)
(12a)	(21a)	60 (1 : 3)	EtOH	1.30 and 1.37 (9 H, each s, 1 : 1 ratio, CO_2CH_2Me), 2.38—2.96 (4 H, m, 2 × CH_2), 3.20br (1 H, qt, *J* 8 and 2, 1-H), 3.35—3.77 (1 H, m, 4-H), 4.27 (6 H, m, OCH_2)	311 (M^+, 11), 266 (100), 238 (40), 210 (22), 194 (21), 193 (23), 165 (27)
(12b)	(21b)	62 (1 : 3)	EtOH	1.26 (9 H, t, CO_2CH_2Me), 1.84—2.72 (6 H, m, 3 × CH_2), 2.94br (1 H, qt, *J* 8, 1-H), 4.15 (2 H, q, OCH_2), 4.21 (4 H, q, OCH_2)	286 (M^+, 1.9), 241 (48), 173 (46), 167 (77), 166 (62), 140 (57), 139 (100), 111 (46), 67 (90)
(12c)	(21c)	63 (1 : 3)	MeOH	2.35 (1 H, t, *J* 7.5) 2.45 (1 H, dd, *J* 14 and 6.5), 2.72—3.50 (3 H, m,) 3.58—3.90 (1 H, m), 3.70, 3.73, and 3.79 (12 H, each s, CO_2Me)	(at 25 eV), 302 (M^+, 0). 271 (65), 270 (22), 243 (45), 210 (36), 183 (64), 151 (100), 145 (50)
(12d)	(21d)	77 (1 : 1)	EtOH	1.30 and 1.36 (each 3 H, each t, CO_2CH_2Me), 2.40—3.05 (4 H, m, 2 × CH_2), 3.20br (1 H, qt, *J ca.* 7, 1 H), 3.52 (1 H, dd, *J* 10 and 9, 4-H), 4.22 (2 H, q, OCH_2), 4.33 and 4.34 (2 H, each q, 1 : 1 ratio, OCH_2)	246 (M^+, 7), 219 (63), 218 (50), 191 (62), 164 (62), 163 (58), 123 (39), 92 (100), 55 (42)
(12e) (12f)	(21e) (21f)	63 (1 : 1)	EtOH	1.30 and 1.38 (each 3-H, each t, CO_2CH_2Me), 2.28—2.92 4 H, m, 2 × CH_2), 3.16—3.44 (1 H, m, 1-H), 3.58 (1 H, dd, *J* 10 and 8, 4-H), 4.19 and 4.38 (each 2 H, each q, OCH_2)	264 (M^+, 13), 129 (81), 192 (38), 191 (67), 151 (43), 118 (39), 92 (100), 91 (46), 55 (41)
(19)	(22)	87 (1 : 1)	MeOH	2.96—3.44 (5 H, m, 2 × CH_2 and 1-H), 3.74 (3 H, s, CO_2Me), 3.80 (6 H, s, CO_2Me)	242 (M^+, 1.4), 211 (12), 210 (44), 183 (8), 152 (10), 151 (100), 95 (8), 79 (9)

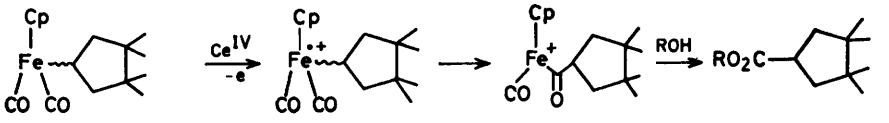
[a] All the products showed a strong absorption at *ν ca.* 1 730 cm^{-1} (C=O, ester). [b] Values in the parentheses given after the yield are the ratios of ether–light petroleum used as eluant.



(12) (21)



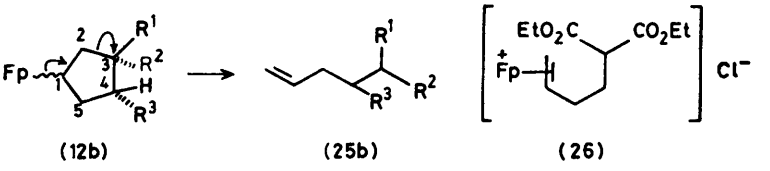
(19) (22)



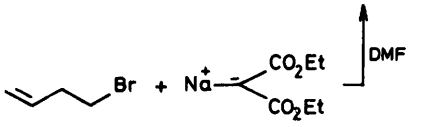
(23) (24)

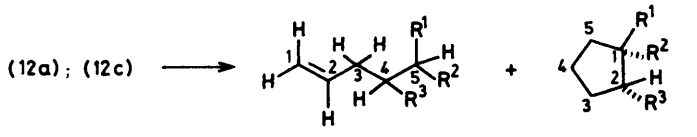
	R^1	R^2	R^3
a;	CO_2Et	CN	CO_2Et
b;	CO_2Et	CO_2Et	H
c;	CO_2Me	CO_2Me	CO_2Me
d;	CN	CN	CO_2Et
e;	CO_2Et	CN	CN
f;	CN	CO_2Et	CN

SCHEME 4 *Reagents:* i, Ce^{IV}, ROH–CO (R = Et or Me)

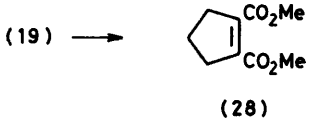


(12b) (25b) (26)





(12a); (12c) (25a); (25c) (27a); (27c)



(28)

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

SCHEME 5

TABLE 4

Acid cleavage of the cyclopentyl-Fp complexes (12a)—(12c) and (19)

Fp-adduct	Yield (%)	Products	Spectral data: ^{1}H N.m.r. chemical shift (δ, J in Hz)	Spectral data: *M/e* (% abundance)
(12a)	61	(25a) : (27a), 1 : 2	1.30 and 1.36 (18 H, each t, CO_2CH_2Me), 1.80—2.74 [14 H, m, CH_2 of (25a) and 3 × CH_2 of (27a)], 3.07—4.00 [4 H, m, 4-H and 5-H of (25a) and 2-H of (27a)], 4.06—4.44 (12 H, m, OCH_2), 5.07—5.36 [2 H, m, HC=CH_2 of (25a)], 5.50—5.90 [1 H, m, H_2C=CH of (25a)]	(at 25 eV), 239 (M^+, 4), 194 (30), 166 (28), 127 (39), 122 (37), 99 (33), 94 (100), 93 (26), 67 (27)
(12b)	67	(25b)	1.27 (6 H, t, CO_2CH_2Me), 2.05 (4 H, m, 2 × CH_2), 3.35 (1 H, t, J 7, CH_2CHCO_2Et), 4.20 (4 H, q, OCH_2), 4.93—5.15 (2 H, m, CH=CH_2), 4.77—4.99 (1 H, m, CH_2CH=CH_2)	214 (M^+, 0), 160 (92), 133 (30), 123 (20), 120 (55), 119 (27), 95 (27), 67 (100), 57 (32)
(12c)	70	(25c) : (27c), 1 : 1	1.57—2.70 [8 H, m, CH_2 of (25c) and 3 × CH_2 of (27c)], 3.10—3.90 [3 H, m, 4-H and 5-H of (25c) and 2-H of (27c)], 3.67, 3.71, 3.73, and 3.7 [18 H, each s, OMe of (25c) and (27c)], 4.94—5.16 [2 H, m, HC=CH_2 of (25c)], 5.50—5.93 (1 H, m, H_2C=CH of (25c)]	244 (M^+, 0), 213 (13), 89 (45), 87 (25), 73 (26), 59 (40), 57 (32), 45 (100), 44 (31), 43 (69)
(19)	75 [a]	(28)	1.98br (2 H, qt, J 7.5, CH_2), 2.73 (4 H, t, J 7.5, 2 × CH_2), 3.86 (6 H, s, OMe)	184 (M^+, 10), 153 (100), 152 (75), 93 (47), 67 (52), 66 (55), 57 (51), 55 (48), 41 (58)

[a] Ref. 24.

the attack of proton, such that the ring-opening process becomes less favourable (Scheme 5).

The cyclic derivative (28) was the exclusive product obtained from the reaction of the DMAD adduct (19) with HCl. The spectral data for this compound was identical with that reported for dimethyl cyclopentene-1,2-dicarboxylate.[24]

(iii) *Bromination.* *N*-Bromopyridinium bromide has been used as an effective brominating agent for the cleavage of primary alkyl-Fp derivatives.[3] When the adducts (12a)—(12c) were treated with this reagent (1—2 molar excess) in CH_2Cl_2 at −70 °C and −20 °C followed by warming to room temperature a mixture of the brominated cyclopentane derivatives (29) and the olefins (30) (Scheme 6) was formed. The yields and reaction conditions are summarised in Table 5.

TABLE 5

Bromination of the cyclopentyl-Fp complexes (12a)—(12c)

Fp-adduct	Mol equiv of brominating agent added: *T* −70 °C	*T* −20 °C	Yield (%)	Product ratio (%) [c] (29) : (30)	Spectral data: ^{1}H N.m.r. chemical shift (δ, J in Hz)	Spectral data: *M/e* (% abundance)
(12a)	1.5	1.5 [a]	32	3 : 2	(29a) Isomer A 1.30 and 1.39 (each t, CO_2CH_2Me), 2.40—3.24 (4 H, m, 2 × CH_2), 3.99 (1 H, dd, J 10 and 8, 4-H), 4.14—4.68 (5 H, m, OCH_2 and 1-H)	(at 25 eV), 319, 317 (M^+, 3), 274, 272 (12 and 14), 238 (14), 198 (28), 174 (35), 172 (37), 93 (25), 92 (100), 65 (43)
					(29a) Isomer B 1.30 and 1.37 (each 3 H, each t, CO_2CH_2Me), 2.44—3.07 (4 H, m, 2 × CH_2), 3.49 (1 H, dd, J 12 and 7, 4-H), 4.10—4.50 (5 H, m, OCH_2 and 1-H)	319, 317 (M^+, 0), 274, 272 (8 and 10), 174 (19), 172 (19), 164 (21), 120 (15), 93 (16), 92 (68)
					(30a) 1.30 and 1.37 (each 3 H, each t, CO_2CH_2Me), 2.44—3.07 (2 H, CH_2), *ca.* 3.68 (1 H, m, $CHCO_2Et$), 4.10—4.50 (4 H, m, OCH_2), 5.66—6.30 (2 H, CH=CH)	
(12b)	2 [b]		85	13 : 7	(29b), 1.26 and 1.27 (each 3 H, t, CO_2CH_2Me), 2.03—3.08 (6 H, m, 3 × CH_2), 4.09—4.35 (4 H, m, OCH_2), 4.38 (1 H, qt, J 5.5, CHBr)	(29b) and (30b) 249, 247 [11, (29b) — OEt)] 213 [(30b), (29b) — Br], 173 (53), 139 [68, (30b) — CO_2Et], 111 (39), 89 (45), 67 (83), 45 (100), 44 (33)
	1 [a]	1	76	13 : 7	(30b) 1.26 and 1.27 (each 3 H, t, CO_2CH_2Me), 2.03—3.08 (4 H, m, 2 × CH_2), 4.09—4.35 (4 H, m, OCH_2), 5.60—6.06 (2 H, m, CH=CH)	
(12c)	1 [b]	1	29	3 : 1	(29c) 2.16 and 3.33 (4 H, m, 2 × CH_2), *ca.* 3.58 (1 H, m, 4-H), 3.72, 3.75, 3.79, and 3.82 (9 H, each s, CO_2Me), 4.08 and 4.17 (1 H, each t, J 8.5, 1 : 1 ratio, 1-H)	(29c) and (30c) 293, 291 [21 and 20, (29c) — OMe], 292 and 290 [14 and 13, (29c) — HOMe], 211 [77, (30c) — OMe], 171 (25), 151 (100), 93 (24), 69 (60), 65 (31), 59 (59)
	1 [a]	1	43		(30c) 2.16—3.33 (2 H, m, CH_2), *ca.* 3.58 (1 H, m, $CHCO_2Me$), 3.72, 3.75, 3.79, and 3.82 (9 H, each s, CO_2Me), 4.31—4.69 (2 H, m, CH=CH)	

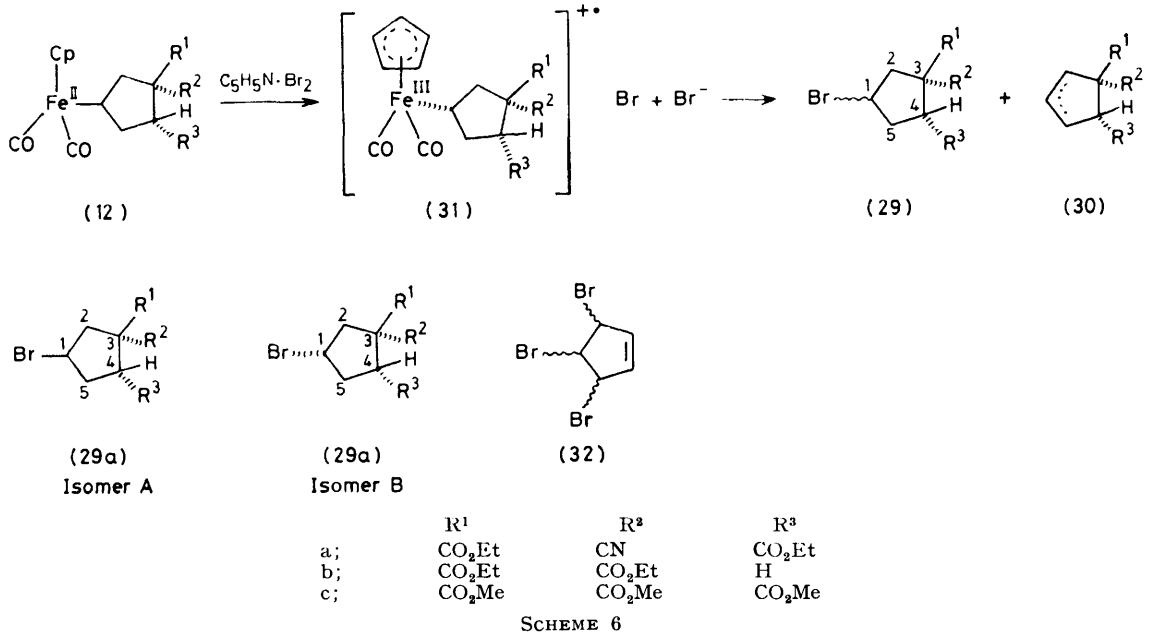
[a] Method (*ii*). [b] Method (*i*). [c] Estimated from the n.m.r. spectrum of the mixture, as the compounds were not separable on column chromatography.

It has been postulated [25,26] that bromolysis of the iron–carbon bond involves the initial formation of the iron radical-cation (31) (Scheme 6) by an oxidative process. This in turn could undergo direct attack either by the bromine radical or anion. Steric factors may disfavour this process, however, with the cyclopentyl-Fp complexes, resulting in the elimination of FpH.

The brominated product (29a) was isolated as a mixture of the two isomers A and B which were partially separated by rapid chromatography [27] on silica gel. products (29a), (29c), (30a), and (30c) were too similar to that of FpBr on neutral alumina, silica gel, and Florisil.

(iv) *β-Hydride abstraction.* Conversion of the alkyl-Fp complexes into the corresponding Fp-(η^2-olefin) cations by treatment with trityl tetrafluoroborate followed by liberation of the olefin by the addition of sodium iodide has been widely used [18,31-33] for removal of the Fp-group.

Reaction of the Fp-complex (12b) with trityl tetrafluoroborate, followed by the addition of sodium iodide

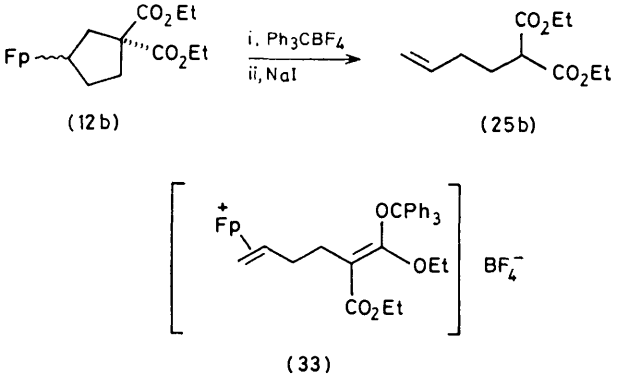


	R^1	R^2	R^3
a;	CO_2Et	CN	CO_2Et
b;	CO_2Et	CO_2Et	H
c;	CO_2Me	CO_2Me	CO_2Me

SCHEME 6

It is probable that the bromination has occurred with inversion of configuration.[26,28,29] 3,4,5-Tribromocyclopentene (32) was the only product isolated, in *ca.* 17% yield, from the reaction of (12d) and (12e) + (12f) with *N*-bromopyridinium bromide. This unusual compound was thought to have arisen from the bromination of the cyclopentadienyl group of the Fp-complex. A similar observation was made earlier with a tricarbonyl(η^5-cyclopentadienyl)rhenium complex.[30]

The low isolated yields obtained in a number of reactions, together with the failure to isolate any of the bromo-product (29) from the bromination of the Fp-complexes (12d) and (12e) + (12f) may be due to the decomposition of the brominated adducts (29) on irradiation with light (to decompose the iron complex), since the crude reaction products [(29, (30), F_pBr, *etc.*) were obtained in high yield (70—100%). In addition, FpBr was separated from the reaction mixture of the Fp-complex (12b) by column chromatography on neutral alumina, as the isolation procedure involving decomposition of the iron complex with light followed by filtration was not required in this case; this could account for the high isolated yield of the products (29b) and (30b). Separation of FpBr from the other compounds could not be effected by this means as the retention times of the resulted in the formation of the malonate (25b) (51%) (Scheme 7). The formation of this linear product probably arises by protonation of the *O*-trityl derivative (33). Alternatively, HBF_4 might have been generated in the reaction mixture and reacted with (12b) in an identical manner to that described for the HCl reaction.



SCHEME 7

EXPERIMENTAL

All operations were performed under an atmosphere of pure, dry nitrogen, using solvents which had recently been dried, distilled, argon purged, and stored under N_2 or argon

over molecular sieves. Ether refers to diethyl ether and light petroleum to the fraction of b.p. 40—60 °C. Melting points were determined using sealed capillary tubes and are uncorrected. The i.r. spectra were taken on a Perkin-Elmer 157 spectrometer, generally as solutions, and absorption values are given in cm^{-1} (s, strong; w, weak; m, medium). ^1H N.m.r. spectra were obtained on a Perkin-Elmer R12A at 60 MHz and at 100 MHz on an XL 100, FT instrument in $CDCl_3$ (unless otherwise stated) with tetramethylsilane as an internal standard [(s), singlet; (d), doublet; (t), triplet; (q), quartet; b, broad]. Mass spectra were run on either an AEI MS12 spectrometer or a Kratos MS30 at an ionization potential of 70 eV (unless otherwise stated). Elemental analyses were recorded by Butterworth Laboratories Ltd., University College, London and I.C.I. Pharmaceuticals Division, Alderley Edge.

Column chromatography was performed with 100—200 mesh silica gel (W. R. Grade Ltd.), neutral alumina (Woelm Act-III—V), or 100—200 mesh Florisil (Floridin). Flash column-chromatography [27] was performed with 230—400 mesh silica gel (Merck, Type 60).

F_p = dicarbonyl (η^5-cyclopentadienyl)iron and Cp = cyclopentadienyl.

(η^1-Allyl)dicarbonyl(η^5-cyclopentadienyl)iron (1).—(i) *Preparation of the Fp-(η^2-propene) tetrafluoroborate salt* (10). To a solution of FpNa [34,35] (60 mmol) in tetrahydrofuran (THF) (100 ml) at 0 °C was added freshly distilled allyl chloride (10 g, 130 mmol) dissolved in THF (10 ml). After being stirred at 0 °C for 15 min, the reaction mixture was allowed to warm to room temperature over 1 h and then concentrated under reduced pressure. The residue was extracted with pentane (*ca.* 400 ml), the extract was filtered through a sinter under a constant pressure of nitrogen, and the solvent was removed under reduced pressure to give (η^1-allyl)-Fp (1) (12.5 g, 96% crude yield). This crude product was dissolved in ether (30 ml) and added as drops to 40% aqueous fluoroboric acid (12 ml, 72 mmol, technical solution) in acetic anhydride (50 ml) at 0 °C. The reaction mixture was stirred at this temperature for 30 min and ether was added to precipitate the Fp-(η^2-propene) tetrafluoroborate salt (10) as a bright yellow solid. This precipitate was collected, washed well with ether (*ca.* 200 ml), and dried under reduced pressure to afford the salt (10) (15.75 g, 86%).

(ii) *Regeneration of (η^1-allyl)-Fp* (1) *from the salt* (10). A solution of the salt (10) (2 g, 6.5 mmol) in dichloromethane (CH_2Cl_2) (20 ml) was cooled to 0 °C and triethylamine (1.45 g, 14 mmol) was added in one portion. After the mixture had been stirred at 0 °C for 30 min and at room temperature for another 30 min, the solvent was removed under reduced pressure and the residue was extracted with pentane (*ca.* 40 ml). The pentane extract was filtered under nitrogen and concentrated to give (η^1-allyl)-Fp (1) in quantitative yield (*ca.* 1.4 g) as an amber oil. This was immediately used for the reactions.

Reactions of (η^1-Allyl)-Fp (1) *with the Electron-deficient Olefins* (11).—*General procedure.* To a solution of the allyl complex (1) (*ca.* 2 mmol) in the appropriate solvent (Table 1) (5—15 ml) was added the unsaturated compound (11) (1—3 equiv.) dissolved in the same solvent. The reaction mixture was then stirred at room temperature for the reaction times indicated (Table 1). After removal of the solvent under reduced pressure [dimethylformamide (DMF) and THF at 0.1 Torr, CH_2Cl_2 and benzene at 14 Torr], the crude product was chromatographed on a 20 mm × 30 cm column. The residue was, in general, applied to the column as a benzene solution. The products were eluted with an ether–light petroleum mixture. In many cases, the products obtained from the column were further purified by recrystallisation. All the products (12) * showed satisfactory spectral and analytical data (Table 2).

(i) *Ethyl 3,3-Dicyanoacrylate* (11d).—To a mixture of freshly distilled malononitrile (27.75 g, 142 mmol) and ethyl glyoxylate (51.0 g, 150 mmol) at 0 °C was added over 15 min a solution of β-alanine (0.6 g, 6.7 mmol) in water (60 ml). Ethanol (*ca.* 90 ml) was then added until the mixture became homogeneous. After being stirred at room temperature for *ca.* 20 h, the resulting solution was poured into water (600 ml) and extracted with ether (4 × 200 ml). The combined extracts were washed with water (200 ml), dried (anhydrous Na_2SO_4), and the solvent was removed under reduced pressure. The residue was flash distilled at 200 °C (0.5—1.0 Torr) and the major fraction collected (26 g), b.p. 80—120 °C. Redistillation afforded the *acrylate* (11d) as an oil (16%), which solidified on cooling, b.p. 90—91 °C/0.5 Torr, m.p. 38—39 °C (from ether–light petroleum) (Found: C, 55.35; H, 4.15; N, 18.55. $C_7H_6N_2O_2$ requires C, 56.00; H, 4.03; N, 18.66%); $\nu_{max.}$ ($CHCl_3$) 2 235 (C≡N), 1 732s, (C=O), and 1 616m (C=C); δ 1.39 (3 H, t, *J* 7 Hz, CO_2CH_2Me), 4.41 (2 H, q, *J* 7 Hz, OCH_2), and 7.16 (1 H, s, C=CH); *m/e* 150 (M^+, 1.1%), 122 (11), 105 (100), 66 (12), and 45 (15).

Reaction of (η^1-Allyl)-Fp (1) *with Dimethyl Acetylenedicarboxylate* (DMAD).—To a solution of the complex (1) (0.470 g, 2.2 mmol) in DMF (5 ml) was added DMAD (0.640 g, 4.5 mmol) and the resulting solution was stirred for 90 h. The solvent was removed under reduced pressure and the residue was chromatographed over neutral alumina (Act-III). When eluted with a mixture of ether–light petroleum (1 : 4), compounds (18) and (20) were obtained as amber oils [93 mg, 12%, ratio of (18) to (20), 9 : 2]. Dicarbonyl(η^5-cyclopentadienyl)(η^1-1,2-diethoxycarbonylpenta-1,4-dienyl)iron (18) showed $\nu_{max.}$ (CCl_4) 2 022, 1 980s (C≡O), 1 700s (C=O, ester), and 1 633m (C=C); δ 3.09 (2 H, dd, *J* 6 and 1.5 Hz, CH_2CH), 3.76 (6 H, s, CO_2Me), 4.77—5.18 (2 H, m, $CH=CH_2$), 4.97 (5 H, s, Cp), and 5.46—6.15 (1 H, m, $CH_2CH=CH_2$); *m/e* (25 eV) 360 (M^+, 0%), 304 (100; $M^+ - 2CO$), 180 (26), 152 (56), 122 (50), 121 (55), 69 (33), 65 (27), and 56 (26). Dicarbonyl(η^5-cyclopentadienyl)(η^1-4,5-diethoxycarbonylpenta-2,4-dienyl)iron (20) showed $\nu_{max.}$ (CCl_4) 2 008 and 1 944s (C≡O); δ 2.14br (2 H, d, *J* *ca.* 5 Hz, CH_2CH), 3.74 (6 H, s, CO_2Me), 4.55—5.15 (2 H, CH=CH), 4.95 (5 H, s, Cp), and 6.87br (1 H, s, $C=CHCO_2Me$).

Further elution with a 33% solution of light petroleum in ether yielded *dicarbonyl(η^5-cyclopentadienyl)(η^1-3,4-ethoxycarbonylcyclopent-3-enyl)iron* (19) as a yellow solid (0.326 g, 42%), m.p. 94—96 °C (Found: C, 52.75; H, 4.5. $C_{16}H_{16}FeO_6$ requires C, 53.36; H, 4.48%); δ 2.40—3.12 (5 H, m, 2 × CH_2 and 1-H), 3.77 (6 H, s, CO_2Me), and 4.81 (5 H, s, Cp); $\nu_{max.}$ ($CHCl_3$) 1 999, 1 945s (C≡O), 1 720s (C=O, ester), and 1 642 m (C=C); *m/e* 360 (M^+, 1.3%), 304 (100, *M* —

* Dicarbonyl(η'-*r*-3-cyano-3,*c*-4-diethoxycarbonylcyclopentyl)-(η^5-cyclopentadienyl)iron (12a), *dicarbonyl(η^5-cyclopentadienyl)-(η'-3,3-diethoxycarbonylcyclopentyl)iron* (12b), *dicarbonyl(η^5-cyclopentadienyl)(η'-3,3,4-trimethoxycarbonylcyclopentyl)iron* (12c), *dicarbonyl(η^5-cyclopentadienyl)(η'-3,3-dicyano-4-ethoxycarbonylcyclopentyl)iron* (12d), *dicarbonyl(η^5-cyclopentadienyl)(η'-r-3,c-4-dicyano-3-ethoxycarbonylcyclopentyl)iron* (12e), *dicarbonyl(η^5-cyclopentadienyl)(η'-r-3,t-4-dicyano-3-ethoxycarbonylcyclopentyl)-iron* (12f), and dicarbonyl(η^5-cyclopentadienyl)(η'-3,3-dimethoxycarbonylcyclopentyl)iron (12g).

2CO), 244 (33), 210 (70), 180 (72), 152 (71), 122 (64), 121 (60), and 56 (32).

Oxidative Carboxylation of the Cyclopentyl-Fp Adducts (12) *and* (19).—*General procedure.* To a solution of the Fp-adduct [(12a)—(12f) and (19)] (*ca.* 0.5 mmol) in either anhydrous methanol or ethanol (previously saturated with carbon monoxide for 2 h) was added ammonium ceric nitrate (4 equiv.) in one portion at room temperature. Carbon monoxide was bubbled through the solution overnight. The solvent was removed under reduced pressure and the residue was diluted with water (50 ml) after which the solution was extracted with benzene (4 × 25 ml). The combined organic extracts were dried (anhydrous Na_2SO_4), after which the solution was filtered and concentrated, and the crude product was chromatographed on Florisil with ether–light petroleum as eluant. The pure oily products (21a)—(21f) and (28) * were obtained in good yields (Table 3) and characterised from spectral data (Table 3).

Acid Cleavage of the Cyclopentyl-Fp Complexes (12a)—(12c) *and* (19).—*General procedure.*—The cyclopentyl-Fp adduct (0.4 mmol) was dissolved in CH_2Cl_2 (40 ml) and hydrogen chloride gas was bubbled through at 0 °C for 1 h. The reaction mixture was then set aside for *ca.* 40 h at room temperature. The solvent was removed under reduced pressure, after which the residue was dissolved in carbon tetrachloride (50 ml) and exposed to sunlight for 3 h (to decompose any FpCl present). The green solid was filtered off and the filtrate was concentrated to give the crude products [(25) and/or (27)] † which were purified by rapid chromatography [27] on silica gel (10 g), 20 mm column].

The products (25a) and (27a), and (25c) and (27c) were obtained as inseparable mixtures and the ratios were determined from the ^1H n.m.r. spectral data (Table 4).

Bromination of Cyclopentyl-Fp Complexes (12a)—(12c).—*General procedure. N*-Bromopyridinium bromide (*ca.* 0.28 mmol) was added in one portion to a solution of the Fp-adduct (12) (0.28 mmol) in CH_2Cl_2 (10 ml) at *ca.* −70 °C. The reaction mixture was stirred at this temperature for 1 h and was then slowly warmed to −20 °C over a period of 3 h. An additional equivalent of brominating agent was added and the reaction mixture allowed to come to room temperature. Two different procedures were used to remove the excess of brominating agent.

(i) The CH_2Cl_2-solution of compound (12b) was filtered and the solvent was removed under reduced pressure, after which chromatography of the residue over neutral alumina (Act-III) afforded a mixture of diethyl 3-bromocyclopentane-1,1-dicarboxylate (29b) and diethyl cyclopent-2 (or 3)-ene-1,1-dicarboxylate (30b) (Table 5).

(ii) The CH_2Cl_2 solution was washed with saturated aqueous sodium thiosulphate (10 ml) followed by back-washing the aqueous layer with CH_2Cl_2 (2 × 10 ml). The organic extracts were combined, washed with saturated aqueous sodium chloride (20 ml), dried, and the solvent removed under reduced pressure. The resulting residue obtained from compound (12b) was chromatographed on neutral alumina (Act-III). Elution with ether–light petroleum (3 : 1) afforded a mixture of compound (29b) and (30b) (Table 5). In cases where the purification of the crude residue by chromatography was not possible [*i.e.* the residue obtained from complexes (12a) and (12c)], the CH_2Cl_2 solution was filtered through neutral alumina (Act-III). The solvent was removed under reduced pressure, after which exposure of the residue in a mixture of ether–light petroleum (50 ml, 1 : 1) to sunlight for 6 h decomposed any FpBr present. This solution was then concentrated and the crude product was chromatographed on neutral alumina (Act-III). Elution with ether–light petroleum (1 : 1) afforded mixtures of diethyl 4-bromo-1-cyanocyclopentane-*r*-1,*t*-2-dicarboxylate (29a) and diethyl 1-cyanocyclopent-4 (or 5)-ene-*r*-1,*t*-2-dicarboxylate (30a), and trimethyl 4-bromocyclopentane-1,1,2-tricarboxylate (29c) and trimethyl cyclopent-4 (or 5)-ene-1,1,2-tricarboxylate (30c) (Table 5).

Bromination of the Iron Complexes (12e) + (12f).—*Isolation of* 3,4,5-*tribromocyclopentene* (32). To a solution of the Fp-adduct (12e) + (12f) (184 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) at −70 °C was added *N*-bromopyridinium bromide (239 mg, 1.0 mmol) in one portion. The reaction mixture was then allowed to warm to −15 °C and a further 2 equiv. of brominating agent was added. After the solution had been stirred at room temperature for 20 h, the i.r. spectrum of the reaction mixture indicated completion of the reaction. The solution was filtered through Florisil (2 mm × 5 cm column), with CH_2Cl_2 as eluant and the solvent was removed under reduced pressure. The residue was then dissolved in ether (50 ml) and exposed to sunlight for 3 h to decompose any FpBr present. After filtration and removal of the solvent under reduced pressure, the crude product was purified by rapid chromatography [silica gel (6 g), 10 mm column)] with ether–light petroleum (3 : 2) as eluant to give 3,4,5-tribromocyclopentene (32) (26 mg, 17%); $\nu_{max.}$ 1 600 (C=C); δ 4.94br (1 H, s, CHBr*CH*Br*CH*Br), 5.15br (2 H, s, *CH*BrCHBr*CH*Br), and 6.13br (2 H, s, CH=CH); *m/e* 306 (0.4%), 304 (0.4), 227 (49), 225 (100), 223 (54), 146 (39), 145 (16), 144 (39), and 143 (15). In addition to compound (32), a mixture of unidentifiable derivatives (19 mg) was also isolated from the above column.

β-*Hydride Abstraction followed by Olefin Liberation of the Complex* (12b).—A solution of trityl tetrafluoroborate (0.140 g, 0.42 mmol) in CH_2Cl_2 (2 ml) was added as drops to a solution of the Fp-adduct (12b) (0.166 g, 0.43 mmol) in the same solvent (3 ml) at 45 °C. After being stirred for 2 h at this temperature the reaction was complete (*vide* i.r. spectrum). The reaction mixture was cooled to 0 °C and the resulting Fp-(η^2-olefin) salt was precipitated by addition of ether (*ca.* 30 ml). The solvent was decanted off and the residue was washed with ether and dried under reduced pressure to give the salt (0.134 g, 66%); $\nu_{max.}$ (CH_2Cl_2) 2 075 and 2 035 s (C≡O).

The above salt was taken up in acetone (2 ml) and sodium iodide (85 mg, 0.57 mmol) was added, in one portion, after which the solution was stirred and the resulting mixture was kept at room temperature for 1 h. The solvent was removed under reduced pressure, after which the residue was extracted with CH_2Cl_2 (*ca.* 10 ml) and the extracts were filtered (to remove the excess of sodium iodide) and concentrated. The crude product obtained was dissolved in carbon tetrachloride (20 ml), after which the solution was

* Triethyl 1-cyanocyclopentane-*r*-1,*t*-2,4-tricarboxylate (21a), triethyl cyclopentane-1,1,3-tricarboxylate (21b), tetramethyl cyclopentane-1,1,2,4-tetracarboxylate (21c), diethyl 4,4-dicyanocyclopentane-1,3-dicarboxylate (21d), diethyl 1,*t*-5-dicyanocyclopentane-*r*-1,3-dicarboxylate (21e), diethyl 1,*c*-5-dicyanocyclopentane-*r*-1,3-dicarboxylate (21f), and dimethyl cyclopent-1-ene-1,2-dicarboxylate (28).

† Diethyl 1-cyanopent-4-ene-1,2-dicarboxylate (25a), diethyl pent-4-ene-1,1-dicarboxylate (25b), trimethyl pent-4-ene-1,1,2-tricarboxylate (25c), diethyl 1-cyanocyclopentane-*r*-1,*t*-2-dicarboxylate (27a), and trimethyl cyclopentane-1,12-tricarboxylate (27e).

exposed to sunlight for 3 h (to decompose any IpI present), filtered, and the solvent removed under reduced pressure. The residue was purified by rapid chromatography [27] [silica gel (10 g), 20 mm column), with ether–light petroleum (1 : 4) as eluant, to yield the malonate [23] (25b) (**46** mg, 51%).

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