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

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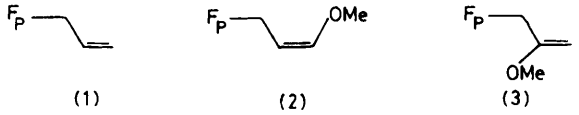
Dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxyallyl)iron (3) has been treated with a number of tetra-, tri-, and di-substituted electron-deficient olefins and acetylenes. A mixture of cyclic and linear products has been formed from reaction of complex (3) with trimethyl ethylenetricarboxylate and diethyl 1-cyanoethylene-1,2-dicarboxylate, with exclusive formation of the cyclopentyl-Fp adduct from ethyl 3,3- and 2,3-dicyanoacrylates. Reaction of complex (3) with tetramethyl ethylenetetracarboxylate, its tetraethyl analogue, diethyl methylenemalonate, t-butylcyanoketen, and dimethyl acetylenedicarboxylate has given, on the other hand, only linear adducts arising from H-transfer. Demetallation of the ($\eta^1$-3,3-dicyano-4-ethoxycarbonyl-1-methoxycyclopentyl)-Fp complex (6b) with ceric ammonium nitrate and carbon monoxide has given a mixture of the corresponding cyclopentanone dimethyl acetal and olefin derivatives.

We have, in the previous papers, reported reactions of ($\eta^1$-allyl)dicarbonyl($\eta^5$-cyclopentadienyl)iron (1) [1] and its (3-methoxyallyl) analogue (2) [2] with a variety of electron-deficient alkoxycarbonyl- and cyano-substituted olefins and acetylenes. It was observed that these allyl complexes usually yielded the corresponding cyclopentyl-Fp adducts [Fp = $Fe(CO)_2$(cyclopentadienyl)], from which the cyclopentane derivatives were liberated by various demetallation reactions. The reactivity of allyl complexes in these cycloadditions was dependent on the electron density on the allyl complex. With a view to obtaining a more reactive complex, ($\eta^1$-2-methoxyallyl)-Fp (3) was prepared [3] as a fairly stable amber oil and the results of the reactions of complex (3) with a number of electron-deficient olefins and acetylenes are now reported.




(1) (2) (3)

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

## RESULTS AND DISCUSSION

Dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxyallyl)-iron (3) was prepared as reported earlier [3] and reactions with a number of olefins studied (Table). Reactions of complex (3) with trimethyl ethylenetricarboxylate (4a) [4,5] (1 equiv.) in dimethylformamide (DMF) yielded, after column chromatography (neutral alumina), three 1 : 1 adducts in a ratio of *ca.* 6 : 1 : 3, together with $FpCH_2COMe$ (11) (Scheme 1). In this reaction it is feasible that the collapse of the intermediate zwitterion (5) (Scheme 1) could follow several routes; (*a*) cyclisation, (*b*) H-transfer, and (*c*) insertion. The latter two processes would give rise to the linear products which could, in turn, be hydrolysed on the column to afford complexes (9a) and (10a) (Scheme 1). From the spectral data, the three adducts obtained above were assigned the structures (6a), (7a), and (9a), respectively, for the following reasons. In the $^1$H n.m.r. spectrum the resonances due to the $CH_2$-, methoxy-, and cyclopentadiene (Cp)-groups of the adduct (7a) were comparable with those of (2-methoxyallyl)-Fp (3). The stretching frequencies of the olefinic bond and carbon monoxide in the i.r. spectrum of complex (7a) were also comparable with those of complex (3), indicating the close similarity in the structure. The spectra of cyclopentyl-Fp adduct (6a) were similar to the analogous cyclic adduct reported earlier.[3] The spectral features of complex (9a) were almost the same as those of $FpCH_2COMe$ (11), which was always isolated as a side-product in the reactions of complex (3) because of hydrolysis. The hydrolysis of complex (7a) might be taking place during purification by column chromatography, as the $^1$H n.m.r. spectrum of the crude reaction mixture showed no hydrolysed product (9a), but this was formed exclusively in 38% yield by treatment of an aqueous tetrahydrofuran (THF) solution of the crude reaction mixture with toluene-*p*-sulphonic acid.

It has been found that solvent polarity influences the reaction pathway, since the H-transfer adduct (7a) was the only product formed when the reaction was conducted in THF and benzene. In contrast, a mixture of the two adducts (6a) and (7a) was formed in DMF and $CH_2Cl_2$. The reaction was faster in the more polar DMF and $CH_2Cl_2$ than in THF and benzene.

The Fp-complex (6b) was the sole product obtained from the reaction of ethyl 3,3-dicyanoacrylate (4b) [1] with the alkyl complex (3) in DMF at room temperature for 3 h. The yellow, solid adduct, isolated in yields of 45 and 32% after column chromatography on Florisil and neutral alumina, respectively, was further purified by recrystallisation. The low yield for this reaction was probably due to decomposition of the product during chromatography, as the $^1$H n.m.r. spectrum of the crude product indicated a quantitative conversion into complex

† Part 2, preceding paper.

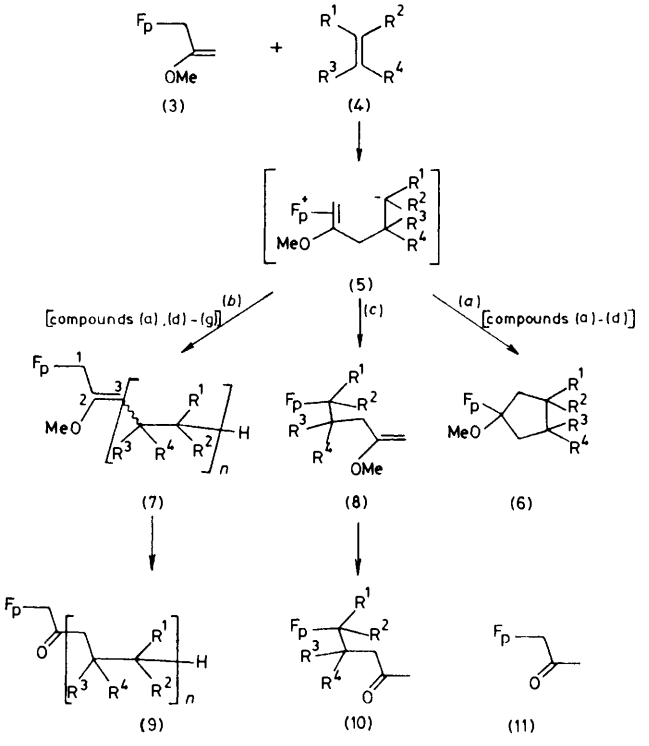
Reactions of (2-methoxyallyl)-Fp-complex (3) with electron-deficient olefins

| Olefin (4) | Solvent | Reaction time (h) | Product yield (%) [a] | Product ratio (%) (6) | (7) | (9) |
|---|---|---|---|---|---|---|
| *a* | $CH_2Cl_2$ | 20 | 56 [b] | 41 | 50 | 9 |
| | DMF | 2 | 49 [b] | 22 | 47 | 31 |
| | THF | 8 | 53 [b] | 6 | 79 | 15 |
| | $C_6H_6$ | 8 | 61 | 13 | 82 | 5 |
| *b* | $CH_2Cl_2$ | 20 | 58 | 100 | | |
| *c* | $CH_2Cl_2$ | 1 | 71 | 100 | | |
| *d* | $CH_2Cl_2$ | 2.5 | | 2 | *d* | *d* |
| *e* | DMF | 48 | 16 | | | 100 |
| *f* | DMF | 70 | 39 [c] | | | 100 |
| | DMF | 70 | 13 | | 100 | |
| *g* | DMF | 20 | | *e* | *e* | *e* |
| | $C_6H_6$ | 20 | | | | 30 [f] |

[a] Isolated yields. [b] Yields averaged over three reactions. [c] Crude product treated with aqueous THF containing toluene-*p*-sulphonic acid before chromatography. [d] A mixture of simple and polymeric products. [e] Polymer. [f] With polymeric products.

(6b). The yields were further improved to 58% by utilising $CH_2Cl_2$ as solvent.

Reaction of complex (3) with ethyl 2,3-dicyanoacrylate [6] in $CH_2Cl_2$ at room temperature afforded the Fp-complex (6c), as a mixture of diastereoisomers. This was indicated by the presence of a number of methoxy-resonances in its $^1H$ n.m.r. spectrum. When treated with (2-methoxyallyl)-Fp (3) in $CH_2Cl_2$, diethyl 1-cyanoethylene-1,2-dicarboxylate (4d) * yielded a mixture of the linear (7d) and cyclic (6d) products. The $^1H$ n.m.r. spectrum indicated several cyclopentadienyl resonances, probably due to the formation of polymeric species. Considerable problems were encountered in the isolation and purification of the products obtained from this reaction, as chromatography on neutral alumina (Act-III) afforded only $FpCH_2COMe$ (11), with the bulk of the product remaining at the top of the column. Three fractions were, however, isolated from the column using neutral alumina (Act-IV). The first contained polymeric H-transfer adducts (7d, $n = 2$, 3, *etc.*) (*ca.* 14%) and the cyclic adduct (6d) (*ca.* 2%); $FpCH_2COMe$ (11) and the hydrolysed H-transfer adduct (9d) were found in the second and third fractions, respectively. When the crude reaction mixture was treated with aqueous THF and toluene-*p*-sulphonic acid, complex (9d) was isolated in 17% yield in addition to a mixture of complex (11) (*ca.* 13%) and complex (6d) (*ca.* 6%). By using either neutral alumina (Act-V) or Florisil column, the polymeric hydrolysed product (9d, $n = 1$, 2, *etc.*) was isolated in low yield. Thus, in reaction of compound (4d) with the (2-methoxyallyl)-Fp complex (3) the H-transfer process is favoured over cyclisation with formation of considerable amounts of polymeric species.




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| a; | $CO_2Me$ | $CO_2Me$ | H | $CO_2Me$ |
| b; | CN | CN | H | $CO_2Et$ |
| c; | $CO_2Et$ | CN | H | CN |
| d; | CN | $CO_2Et$ | H | $CO_2Et$ |
| e; | $CO_2Et$ | $CO_2Et$ | $CO_2Et$ | $CO_2Et$ |
| f; | $CO_2Me$ | $CO_2Me$ | $CO_2Me$ | $CO_2Me$ |
| g; | $CO_2Et$ | $CO_2Et$ | H | H |
| h; | $CO_2Me$ | $CO_2Me$ | H | H |

SCHEME 1 $n - 1$ unless stated otherwise in the text.

Reaction of complex (3) with tetramethyl ethylene-tetracarboxylate (4e) and its ethyl analogue (4f) [7] at room temperature afforded, exclusively, the linear H-transfer adducts (7e) and (7f), respectively, which were partly hydrolysed on the column during purification. The best yields of complexes (9e) and (9f) were obtained, however, from reactions performed in DMF using an excess of olefin followed by hydrolysis of the crude product with toluene-*p*-sulphonic acid in aqueous THF.

Simple and polymeric H-transfer products (7g, $n = 1$, 2, 3, *etc.*) were isolated from the reaction of complex (3) with diethyl methylenemalonate (4g) in DMF. These products were partly hydrolysed during chromatography. When the reaction was performed in benzene with olefin (1 equiv.), two fractions were isolated from the column.

* Prepared by the procedure described for its dimethyl analogue, see H. K. Hall, jun., and P. Ykman, *J. Am. Chem. Soc.*, 1975, **97**, 800.

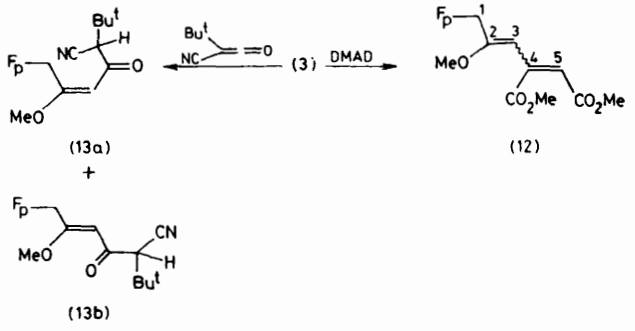
The first contained polymeric, unhydrolysed, H-transfer adducts (7g, $n = 2, 3$, *etc.*), whilst the second fraction consisted of an inseparable mixture (1 : 3) of complexes (11) and (9g), the latter isolated in *ca.* 30% yield. $FpCH_2COMe$ (11) was the only product obtained from the reaction of dimethyl methylenemalonate (4h) with complex (3) in DMF, THF, or diethyl ether. By performing the reaction in benzene, however, the polymeric H-transfer adduct (7h, $n = 2, 3$, *etc.*) was obtained along with complex (11).

From the above reactions it can be concluded that (2-methoxyallyl)-Fp (3) is more reactive when compared with the complexes ($\eta^1$-allyl)-Fp (1) and (3-methoxyallyl)-Fp (2). No reaction was observed between the latter two complexes and tetramethyl ethylenetetracarboxylate (4f). In the majority of cases, H-transfer products were formed either exclusively or in addition to the cyclic products, in contrast with the formation of only cyclic products from complexes (1) and (2). This might be because of the increased stability of the intermediate zwitterion (5) due to the mesomeric electron-donating capacity of the methoxy-group, for which processes other than ring closure may then become important. Cyclisation is additionally disfavoured on steric grounds as metal quaternary bonds are formed and also since the considerable steric bulk of the ester groups might hinder the ring closure. Thus, H-transfer becomes the predominant process with olefins containing more than one ester group [*e.g.* (4a) and (4e)—(4h)]. This steric requirement is reduced, however, by the presence of cyano-groups as in compounds (4b) and (4c), such that cyclisation becomes the preferred process. Formation of considerable quantities of polymeric H-transfer adducts may be due to the presence of an excess of olefin in the reaction mixture.

Reaction of complex (3) with dimethyl acetylenedicarboxylate (DMAD) in DMF at room temperature gave a single product, which was further purified by chromatography on neutral alumina. This adduct was assigned the structure of the H-transfer product (12) from its $^1H$ n.m.r. spectrum, which indicated the presence of two dissimilar olefinic protons, together with vinylic methoxy- and $FpCH_2$-groups. It is interesting to note that this product does not hydrolyse during chromatography, presumably because of the extended conjugation of the enol ether.

Addition of a solution of t-butylcyanoketen, generated in benzene, to complex (3) resulted in the exclusive formation of the linear Fp-complex (13) (Scheme 2). The $^1H$ n.m.r. spectrum of the crude product contained two signals each due to t-butyl, cyclopentadienyl, and vinylic methoxy-resonances, in a 3 : 2 ratio, probably due to the existence of the two isomers (13a) and (13b). Column chromatography on neutral alumina, however, caused the isomerisation of the major product to the minor one, isolated in 63% yield. Since the *trans*-configuration is likely to be the more stable of the two, due to the possible dipolar interactions between methoxy- and ketone-groups, the major product obtained from the reaction might be the *cis*-isomer (13a), which isomerised to the thermodynamically more stable *trans*-isomer (13b) on the column. As with the DMAD product (12), no hydrolysis of the adducts occurred during chromatography.

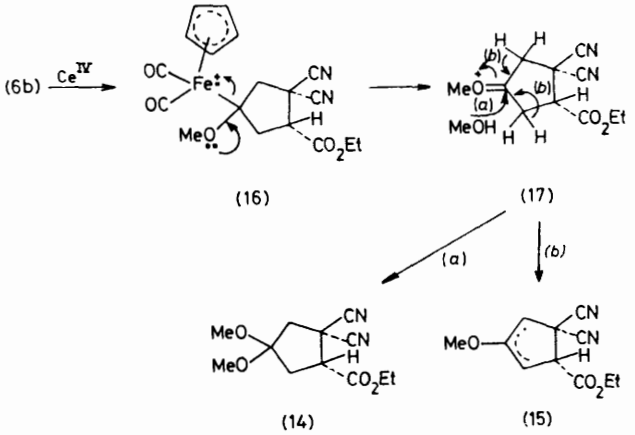
No products were isolated from the reaction of complex (3) in DMF with methyl acrylate, acrylonitrile, *trans*-1,2-dicyanoethylene, methyl cinnamate, ethyl 3-nitroacrylate, β-nitrostyrene, maleic anhydride, *p*-quinone,




SCHEME 2

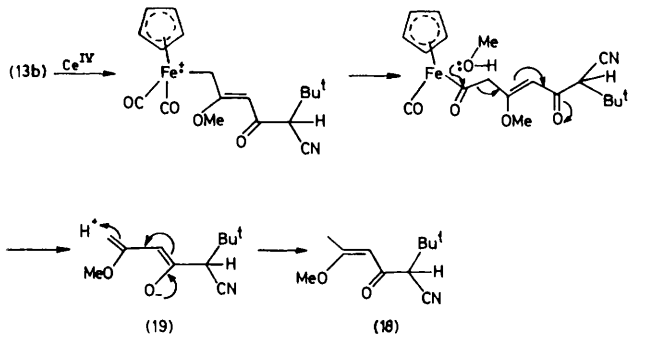
methyl propiolate, and bistrimethylsilylacetylene, even by using an excess of olefin and longer reaction times.

*Demetallation reactions.*—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 [10,11] and ceric salts.[12,13] When a solution of the Fp-complex (6b) (Scheme 1) in methanol (saturated with carbon monoxide) was treated with ceric ammonium nitrate, two products were obtained. On the basis of spectral data, the structures were assigned as the ethyl carboxylate (14) and the olefin (15), in a ratio of 9 : 1 (Scheme 3). This reaction might have proceeded *via* the intermediate (16), formed by abstraction of an electron from iron, followed by loss of the Fp-group to give complex (17). This could either undergo attack by methanol to give compound (14) or collapse through the loss of proton to give compound (15) (Scheme 3).




SCHEME 3

Similar treatment of complex (13b) with ceric salt, however, resulted in the formation of the heptenone (18) in 95% yield. This replacement of Fp with a proton may have proceeded *via* the intermediate enolate anion (19) by the mechanism given (Scheme 4).




SCHEME 4

Thus, the Fp-group in the adducts obtained from (2-methoxyallyl)-Fp (3) in the presence of ceric salt can be replaced by either a methoxy-group or a hydrogen atom. This is in contrast with the reactions of cyclopentyl-Fp adducts obtained from complexes (1) and (2) where the Fp-moiety is replaced by an ester function. This might be due to the presence of a methoxy-group in the products obtained from complex (3) which could hinder the insertion of a carbonyl group into the Fe–C bond.

## EXPERIMENTAL

All operations were carried out as described earlier.[1] Fp = $Fe(CO)_2$(cyclopentadienyl), Cp = cyclopentadienyl, ether refers to diethyl ether, and ν is given in $cm^{-1}$.

*Reactions of Dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxyallyl)iron* (3) *with the Olefins* (4) *and Acetylenes.—General procedure.* To a solution of the allyl complex (3) in the appropriate solvent was added olefin dissolved in the same solvent. The reaction mixture was then stirred at room temperature for the reaction times indicated below. After removal of the solvent under reduced pressure [dimethylformamide (DMF) and tetrahydrofuran (THF) at 0.1 Torr and $CH_2Cl_2$ and benzene at 14 Torr, the crude product was chromatographed on either neutral alumina or Florisil (*ca.* 30 g), employing a 2 cm × 30 cm column. The residue was applied to the column as a benzene solution (2—5 ml) followed by elution with light petroleum and light petroleum–ether.

(a) *Trimethyl ethylenetricarboxylate* (4a).[4,5] (*i*) The reaction of the allyl complex (3) (490 mg, 2.0 mmol) with compound (4a) (800 mg, 4.0 mmol) was carried out in $CH_2Cl_2$ (20 ml) for 20 h, employing the general procedure. Column chromatography of the crude product on neutral alumina (Act-III) resulted in isolation of the following products.

Elution with ether–light petroleum (2 : 3) yielded dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-oxopropyl)iron (11), (30 mg, 6%) and dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxy-4,5,5-trimethoxycarbonyl(pent-2-enyl)iron (7a) (245 mg, 28%) as an unstable amber oil. Complex (11) gave $\nu_{max.}$ ($CCl_4$) 2 030, 1 960s (C≡O) and 1 656s (C=O); δ($CDCl_3$) 1.77 (2 H, s, $CH_2$), 2.07 (3 H, s, Me), and 4.83 (5 H, s, Cp). Complex (7a) gave $\nu_{max.}$ ($CHCl_3$) 2 000, 1 955s (C≡O), 1 735s (C=O, ester), and 1 625m (C=C); δ($CDCl_3$) 1.80 and 2.17 (each 1 H, each d, *J* 9.5 Hz, $FpCH_2$), 3.43 (3 H, s, OMe), 3.68, 3.70, and 3.73 (each 3 H, each s, $CO_2Me$), 3.74—4.10 (3 H, m, C=$CHCH_2$), and 4.80 (5 H, s, Cp); *m/e* 450 ($M^+$, 0%), 394 (49, $M^+ - 2CO$), 252 (100), 152 (59), 1122 (33), 121 (62), 111 (24), and 59 (27).

Elution with ether–light petroleum (3 : 2) yielded complex (11) (37 mg, 8%) and dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-1-methoxy-3,3,4-trimethoxycarbonylcyclopentyl)-iron (6a) (200 mg, 22%) as an oil; $\nu_{max.}$ ($CHCl_3$) 2 000, 1 950s (C≡O), and 1 735s (C=O, ester); δ($CDCl_3$) 1.90—3.00br (4 H, m, 2 × $CH_2$), 3.04 (3 H, s, OMe), 3.68 (6 H, s, $CO_2Me$), 3.79 (3 H, s, $CO_2Me$), *ca.* 3.80 (1 H, m, 4-H), and 4.90 (5 H, s, Cp); *m/e* (25 eV) 450 ($M^+$, 0%), 362 (100), 302 (56), 213 (88), 181 (66), 153 (92), 121 (74), and 69 (54).

Elution with ether yielded dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-4,5,5-trimethoxycarbonyl-2-oxopentyl)iron (9a) (44 mg, 5%). This was crystallized in hexane–ether by cooling at −20 °C overnight to give a yellow, air stable, crystalline *solid* (9a), m.p. 66—67 °C; $\nu_{max.}$ ($CHCl_3$) 2 010, 1 970s (C≡O), 1 740s (C=O, ester), and 1 650m (C=O, ketone); δ($CDCl_3$) 1.73 (2 H, t, *J* 1.25 Hz, $FpCH_2$), 2.91 (2 H, t, *J* 5 Hz, $COCH_2$), 3.50 (1 H, m, 4-H), 3.72 (3 H, s, $CO_2Me$), 3.76 (6 H, s, $CO_2Me$), 3.90 (1 H, d, *J* 7.5 Hz, 5-H), and 4.88 (5 H, s, Cp); *m/e* (25 eV) 436 ($M^+$, 0%), 349 (40), 348 (99), 177 (19), 169 (26), 122 (26), 121 (100), and 95 (29) (Found: C, 49.35; H, 4.65. $C_{18}H_{20}FeO_9$ requires C, 49.56; H, 4.62%).

(*ii*) An aqueous THF solution of the crude product was treated with toluene-*p*-sulphonic acid in the following manner. Water (*ca.* 0.5 ml) and toluene-*p*-sulphonic acid (*ca.* 20 mg) were added to a solution of the allyl complex (3) (538 mg, 2.2 mmol) and the olefin (4a) (870 mg, 4.3 mmol) in THF (30 ml), which had previously been stirred at room temperature for 20 h. The mixture was then stirred for a further 6 h at room temperature. After removal of the solvent under reduced pressure the residue was chromatographed as described above to give the hydrolysed H-transfer adduct (9a) (Scheme 1) (36.3 mg, 38%).

(b) *Ethyl 3,3-dicyanoacrylate* (4b).[1] To a solution of the allyl complex (3) (300 mg, 1.2 mmol) in $CH_2Cl_2$ (15 ml) was added compound (4b) (240 mg, 1.6 mmol) in $CH_2Cl_2$ (5 ml). The mixture was stirred for 20 h and the solvent removed under reduced pressure. Chromatography of the residue thus obtained yielded dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-3,3-dicyano-4-ethoxycarbonyl-1-methoxycyclopentyl)iron (6b) as a yellow crystalline solid on elution with ether–light petroleum (1 : 1) (275 mg, 58%). Recrystallisation from hexane–ether yielded the pure *compound* (6b), m.p. 96—98 °C; $\nu_{max.}$ ($CHCl_3$) 2 242w (C≡N), 2 000, 1 960s (C≡O), and 1 735s (C=O, ester); δ($CDCl_3$) 1.35 (3 H, t, $CO_2CH_2Me$), 2.13 (1 H, dd, *J* 14 and 12 Hz, 5-H), 2.63 (1 H, d, *J* 14 Hz, 2-H), 2.81 (1 H, ddd, *J* 14, 6.5, and 3 Hz, 5-H), 3.16 (3 H, s, OMe), 3.26 (1 H, dd, *J* 14 and 3 Hz, 2-H), 3.65 (1 H, dd, *J* 12 and 6.5 Hz, 4-H), 4.30 and 4.31 (2 H, each q, 1 : 1 ratio, $OCH_2$), and 4.92 (5 H, s, Cp); *m/e* 398 ($M^+$, 0.9%), 276 (27), 221 (47), 194 (50), 166 (48), 147 (23), 122 (36), 121 (100), and 56 (27) (Found: C, 53.65; H, 4.6; N, 7.1. $C_{18}H_{18}FeN_2O_5$ requires C, 54.29; H, 4.56; N, 7.04%).

(c) *Ethyl 2,3-dicyanoacrylate* (4c).[6] The general reaction procedure was employed for the reaction of compound (4c) (273 mg, 1.8 mmol) with the allyl complex (3) (450 mg, 1.8 mmol) in $CH_2Cl_2$ (15 ml) for 1 h. The crude product was chromatographed on neutral alumina (Act-IV) and elution

with ether–light petroleum (3 : 1) yielded dicarbonyl ($\eta^5$-cyclopentadienyl)($\eta^1$-3,4-dicyano-3-ethoxycarbonyl-1-methoxycyclopentyl)iron (6c) (460 mg, 64%), isolated as a yellow crystalline solid, m.p. 148—149 °C (from hexane–ether); $\nu_{max.}$ ($CHCl_3$) 2 240w (C≡N), 2 000, 1 960s (C≡O), and 1 747s (C=O ester); δ($CDCl_3$) 1.36 (3 H, t, $CO_2CH_2Me$), 2.35 (1 H, t, *J* 12 Hz, 5-H), 2.64 (1 H, d, *J* 14 Hz, 2-H), 2.78—3.04 (1 H, m, 5-H), 3.06br (1 H, d, *J* 14 Hz, 2-H), 3.18 (3 H, s, OMe), 3.66 (1 H, dd, *J* 12 and 6 Hz, 4-H), 4.36 (2 H, q, $OCH_2$), and 3.91 (5 H, s, Cp) [$^1$H n.m.r. of crude product showed peaks at δ 3.02, 3.18, and 3.28 (each s, ratio *ca.* 3 : 4 : 1, OMe)]; *m/e* (25 eV) 398 ($M^+$, 0%), 186 (17), 147 (38), 122 (34), 121 (100), 95 (19), 56 (37), and 42 (19).

The yields were improved to 71% by chromatography of the crude residue on neutral alumina (Act-V) and elution with ether.

(d) *Diethyl 1-cyanoethylene-1,2-dicarboxylate* (4d) (*see text*). (*i*) Compound (4d) (476 mg, 2.4 mmol) was treated with the allyl complex (3) (600 mg, 2.4 mmol) in $CH_2Cl_2$ (20 ml) for 2.5 h using the general procedure. The crude product was then chromatographed on neutral alumina (Act-IV) to give the following complexes.

Elution with light petroleum–ether (2 : 3) gave a mixture of the polymeric H-transfer adducts (7d, *n* = 2, 3, *etc.*) (*ca.* 110 mg); δ($CDCl_3$) 1.28 and 1.33 (12 H, m, $CO_2CH_2Me$), 3.54 (3 H, s, OMe), 4.22 (8 H, m, $OCH_2$), and 4.82 (5 H, s, Cp) and dicarbonyl($\eta^1$-3-cyano-3,4-diethoxycarbonyl-1-methoxycyclopentyl)($\eta^5$-cyclopentadienyl)iron (6d) (*ca.* 26 mg, 2%); δ($CDCl_3$) 1.26br (6 H, t, $CO_2CH_2Me$), 3.20 (3 H, s, OMe), 4.14 and 4.19 (each 2 H, each q, $OCH_2$), and 4.89 (5 H, s, Cp).

Complex (11) (*ca.* 120 mg, 2%) was obtained on elution with ether–light petroleum (2 : 3).

Dicarbonyl($\eta^1$-5-cyano-4,5-diethoxycarbonyl-2-oxopentyl)($\eta^5$-cyclopentadienyl)iron (9d) was eluted with ether–light petroleum (3 : 1) in 27% yield (280 mg); $\nu_{max.}$ ($CHCl_3$) 2 020, 1 965s (C≡O), 1 740s (C=O ester), and 1 645 (C=O, ketone); δ($CDCl_3$) 1.27 and 1.32 (each 3 H, each t, $CO_2CH_2Me$), 1.78 (2 H, s, $FpCH_2$), 2.90—3.20br (2 H, m, $COCH_2CH$), 3.55 (1 H, m, 4-H), 4.22 (5 H, m, $OCH_2$ and 5-H), and 4.90 (5 H, s, Cp).

All the products were obtained as amber oils. Chromatography of the crude product on either neutral alumina (Act-V) or Florisil and elution with ether–light petroleum (3 : 1) afforded the mixture of the hydrolysed polymeric adducts (9d, *n* = 2, 3, *etc.*) (*ca.* 20%); δ($CDCl_3$) 1.27 and 1.33 (10 H, each t, $CO_2CH_2Me$), 1.78 (2 H, s, $FpCH_2$), 2.98—3.20br (2 H, dd, *J ca.* 4 and 9 Hz, $COCH_2$), 3.40—3.75 (2 H, m, 4-H), 4.23 (5 H, m, $OCH_2$ and 5-H), and 4.90 (5 H, s, Cp).

(*ii*) An aqueous THF solution of the crude product was treated with toluene-*p*-sulphonic acid in the following manner. The product mixture obtained from the reaction of compound (4d) with the allyl complex (3) (330 mg, 1.2 mmol) in dichloromethane (30 ml) was dissolved in THF (10 ml) and stirred with water (1 ml) and toluene-*p*-sulphonic acid (*ca.* 20 mg) for 30 min. After removal of the solvent under reduced pressure, the residue was chromatographed on neutral alumina (Act-IV) and a mixture of complex (11) (42 mg, 13%), the cyclic adduct (6d) (34 mg, 6%) and the adduct (9d) (114 mg, 19%) was obtained on elution with light petroleum–ether.

(e) *Tetraethyl ethylenetetracarboxylate* (4e).[7] The reaction between complex (3) (540 mg, 2.2 mmol) and compound (4e) (2.75 g, 8.7 mmol) was performed in DMF (10 ml) for 48 h employing the standard reaction procedure. The residue was chromatographed on neutral alumina (Act-III) and eluted with ether–light petroleum (3 : 1) to afford a mixture of complex (11) (160 mg, 31%) and dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-4,4,5,5-tetraethoxycarbonyl-2-oxopentyl)-iron (9e) (187 mg, 16%); $\nu_{max.}$ ($CHCl_3$) 2 005, 1 965s (C≡O), 1 730s (C=O, ester), and 1 645m (C=O, ketone); δ($CDCl_3$) 1.28 (12 H, t, $CO_2CH_2Me$), 1.78 (2 H, s, $FpCH_2$), 3.40 (2 H, s, $COCH_2$), 4.28 (8 H, q, $OCH_2$), *ca.* 4.33 (1 H, s, $CHCO_2Et$), and 4.90 (5 H, s, Cp); *m/e* (25 eV) 550 ($M^+$, 0%), 186 (47), 121 (100), 95 (14), 89 (13), 65 (15), and 56 (29).

(f) *Tetramethyl ethylenetetracarboxylate* (4f).[7] A solution of the allyl complex (3) (410 mg, 1.7 mmol) and tetramethyl ethylenetetracarboxylate (4f) (1.7 g, 615 mmol) in DMF (10 ml) was stirred for 70 h at room temperature. After removal of the solvent under reduced pressure, the residue was dissolved in THF (5 ml) and treated with water (0.5 ml) and toluene-*p*-sulphonic acid (20 mg) for 6 h. The reaction mixture was then concentrated and the crude product chromatographed on neutral alumina (Act-III) to give dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-4,4,5,5-tetramethoxycarbonyl-2-oxopentyl)iron (9f) as an amber oil (320 mg, 39%); $\nu_{max.}$ ($CHCl_3$) 2 010, 1 965s (C≡O), 1 740s (C=O, ester), and 1 645m (C=O, ketone); δ($CDCl_3$) 1.78 (2 H, s, $FpCH_2$), 3.49 (2 H, s, $COCH_2$), 3.78 and 3.80 (each 6 H, each s, $CO_2Me$), 4.35 (1 H, s, $CHCO_2Me$), and 4.89 (5 H, s, Cp); *m/e* (25 eV) 494 ($M^+$, 0%), 407 (23), 406 (52), 194 (27), 153 (26), 121 (100), 69 (40), and 59 (29).

Dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxy-4,4,5,5-tetramethoxycarbonylpent-2-enyl)iron (7f) was obtained in 13% yield by carrying out the reaction in DMF followed by chromatography; $\nu_{max.}$ ($CHCl_3$) 2 000, 1 955s (C≡O) and 1 740s (C=O, ester); δ($CDCl_3$) 1.99 (2 H, s, $FpCH_2$), 3.42 (3 H, s, OMe), 3.77 (12 H, s, $CO_2Me$), *ca.* 3.77 (1 H, s, C=CH), 4.45 (1 H, s, $CHCO_2Me$), and 4.83 (5 H, s, Cp).

(g) *Diethyl methylenemalonate* (4g).[8] (*i*) The standard procedure was employed for the reaction of the 2-methoxyallyl complex (3) (550 mg, 2.2 mmol) with compound (4g) (760 mg, 4.4 mmol) performed in DMF (10 ml) for 20 h. Column chromatography of the crude product on neutral alumina (Act-III) and elution with ether–light petroleum (1 : 1) yielded a mixture of the polymeric H-transfer adducts (7g, *n* = 2, 3, *etc.*) (166 mg); $\nu_{max.}$ ($CHCl_3$) 2 000, 1 950s (C≡O), 1 730s (C=O, ester), and 1 660w (C=C); δ($CDCl_3$) 1.26 (13 H, t, $CO_2CH_2Me$), 2.03 (2 H, s, $FpCH_2$) 2.58br (3.5 H, t, *J* 10 Hz, 4-H), 3.41 (3 H, s, OMe), 3.43—4.80 (2 H, m, C=C*H* and 5-H), 4.21 (9 H, q, $OCH_2$), and 4.80, 4.88, and 4.95 (3.5, 1.0, and 0.5 Hs, each s, Cp). Further elution of the column yielded complex (11) (142 mg, 27%, from ether–light petroleum 3 : 2) and finally, elution with ether yielded the hydrolysed polymeric H-transfer adducts (9g, *n* = 2, 3, *etc.*) (188 mg); δ($CDCl_3$) 1.25 (12 H, t, $CO_2CH_2Me$), 1.74 (2 H, s, $FpCH_2$), 1.97—2.50 (5 H, m, $COCH_2CH_2CH$), 2.56 (1.67 H, d, *J* 6 Hz, $CH_2CHCO_2Et$), 3.53br (1 H, bt, *J* 6 Hz, 5-H), 4.21br (8 H, q, $OCH_2$), and 4.88 and 4.96 (0.7 and 4.3 H, each s, Cp).

(*ii*) Column chromatography of the residue obtained by performing the above reaction in benzene (50 ml) on neutral alumina (Act-III) and elution with ether–light petroleum afforded the adducts (7g, *n* = 2, 3, *etc.*) (219 mg), as well as an inseparable mixture of complex (11) (50 mg, 10%) and dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-5,5-diethoxycarbonyl-2-oxopentyl)iron (9g) (265 mg, 29%); $\nu_{max.}$ ($CHCl_3$) 2 010, 1 965s (C≡O), 1 725s (C=O, ester), and 1 635m (C=O, ketone); δ($CDCl_3$) 1.36 (6 H, t, $CO_2CH_2Me$), 1.74 (2 H, s, $FpCH_2$),

2.00—2.50 (4 H, m, 2 × $CH_2$), 3.47 (1 H, t, *J* 6 Hz, $CHCO_2$Et), 4.24 (4 H, q, $OCH_2$), and 4.90 (5 H, s, Cp).

(*iii*) The crude product obtained from complex (3) (280 mg, 1.5 mmol) and diethyl methylenemalonate (316 mg, 1.8 mmol) in benzene (40 ml) was dissolved in THF (5 ml) and treated with water (0.5 ml) and toluene-*p*-sulphonic acid (20 mg) as described in method (d), (*ii*). Chromatography on neutral alumina (Act-III) and elution with ether–light petroleum (3 : 2) gave a mixture of the polymeric ketones (9g, $n$ = 2, 3, *etc.*) and complex (11) (*ca.* 5 : 2, respectively, 11 mg). These adducts (9g, $n$ = 2, 3, *etc.*) were also obtained as exclusive products from the analogous treatment of the adducts (7g, $n$ = 2, 3, *etc.*) with aqueous THF and toluene-*p*-sulphonic acid.

(h) *Dimethyl methylenemalonate* (4h).[8] Dimethyl methylenemalonate (4h) (265 mg, 1.8 mmol) dissolved in benzene (10 ml) was added to a solution of the allyl complex (3) (380 mg, 1.5 mmol) in benzene (30 ml) and the mixture was stirred at room temperature for 20 h. The solvent was then removed under reduced pressure and the residue was chromatographed on neutral alumina (Act-III). Elution with ether–light petroleum (3 : 2) resulted in the isolation of an inseparable mixture of complex (11) (*ca.* 69 mg, 19%) and the polymeric H-transfer products (7h, $n$ = 2, 3, *etc.*) (154 mg); δ($CDCl_3$) 2.05 (2 H, s, $FpCH_2$), 2.57br (4 H, t, *J* 6 Hz, 4 H), 3.41 (3 H, s, OMe), 3.74br (14 H, s, $CO_2$Me, C=CH and 5-H), and 4.82 (5 H, s, Cp).

(i) *Dimethyl acetylenedicarboxylate* (*DMAD*). DMAD (568 mg, 4.0 mmol) was added in one portion to a solution of the allyl complex (3) (500 mg, 2.0 mmol) in DMF (5 ml), and the reaction mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure and the residue was chromatographed on neutral alumina (Act-III). Elution with ether–light petroleum (2 : 3) afforded dicarbonyl($\eta^5$-cyclopentadienyl)($\eta^1$-2-methoxy-4,5-dimethoxycarbonyl(penta-2,4-dienyl)iron (12) as an amber oil (492 mg, 63%); $\nu_{max.}$ ($CH_2Cl_2$) 2 005, 1 960s (C≡O), 1 718s (C=O, ester), and 1 625w (C=C); δ($CDCl_3$) 2.69 (2 H, s, $CH_2$), 3.62 (6 H, s, $CO_2$Me and OMe), 3.70 (3 H, s, $CO_2$Me), 4.89 (5 H, s, Cp), 5.48 (1 H, d, *J* 2.5 Hz, 3-H), and 6.29 (1 H, d, *J* 2.5 Hz, 5-H); *m/e* (25 eV) 390 ($M^+$, 0%), 334 (15, $M^+$ — 2CO), 177 (18), 149 (20), 122 (20), 121 (100), 96 (19), 95 (23), and 56 (32).

(j) *t-Butylcyanoketen.*[9] A solution of 2,5-diazido-3,6-di-t-butyl-*p*-quinone (400 mg, 1.3 mmol) in benzene (10 ml) was refluxed for 2 h to convert the diazide into t-butylcyanoketen (*ca.* 2.5 mmol). This solution was then cooled to room temperature and added in one portion to the allyl complex (3) (450 mg, 1.8 mmol), dissolved in benzene (10 ml). After the mixture had been stirred at room temperature for 2 h, the solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina (Act-III). Elution with ether–light petroleum (1 : 3) afforded *dicarbonyl*($\eta^1$-*5-cyano-2-methoxy-6,6-dimethyl-4-oxohept-2-enyl*)($\eta^5$-*cyclopentadienyl*)*iron* (13b) as a yellow crystalline solid, m.p. 104—105 °C (425 mg, 63%); $\nu_{max.}$ ($CHCl_3$) 2 230w (C≡N), 2 008, 1 966s (C≡O), 1 646w (C=O, ketone), and 1 520s; δ($CDCl_3$) 1.16 (9 H, s, $Bu^t$), 2.55 (2 H, s, $CH_2$), 3.18 (1 H, s, COCH), 3.70 (3 H, s, OMe), 4.90 (5 H, s, Cp), and 5.46 (1 H, s, C=CH); *m/e* (25 eV) 371 ($M^+$, 0%), 315 (21, $M^+$ — 2CO), 186 (58), 139 (36), 121 (54), 99 (100), 59 (43), 57 (46), and 56 (46) (Found: C, 58.3; H, 5.9; N, 3.75. $C_{18}H_{21}FeNO_4$ requires C, 58.24; H, 5.70; N, 3.77%).

*Demetallation Reactions.*—(i) *Complex* (6b). To a solution of complex (6b) (250 mg, 0.63 mmol) in methanol (30 ml) (previously purged with carbon monoxide for 2 h) was added ammonium ceric nitrate (1.4 g, 2.5 mmol) in one portion at room temperature. Carbon monoxide was then bubbled through the solution overnight. The solvent was removed under reduced pressure and the residue was diluted with water (50 ml). This was extracted with benzene (4 × 25 ml), after which the combined organic extracts were dried (anhydrous $Na_2SO_4$), the solution was filtered and the crude product was chromatographed over Florisil. On elution with ether–light petroleum (2 : 3—3 : 2), compounds (14) and (15) were obtained in the ratio 9 : 1 (143 mg, 92%). Ethyl-2,2-dicyano-4,4-dimethoxycyclopentane-1-carboxylate (14) gave $\nu_{max.}$ ($CHCl_3$) 2 250w (C≡N) and 1 738s (C=O, ester); δ($CDCl_3$) 1.36 (3 H, t, $CO_2CH_2$*Me*), 2.16—2.87 (4 H, m, 2 × $CH_2$), 3.24 and 3.26 (each 3 H, each s, OMe), 3.51 (1 H, dd, *J* 11 and 8.5 Hz, $CHCO_2$Et), 4.32 and 4.34 (2 H, each q, 1 : 1 ratio, $OCH_2$); *m/e* 252 ($M^+$, 0%), 221 221 (25, $M^+$ — OMe), 194 (30), 180 (16), 166 (33), 152 (100), 147 (20), 145 (18), and 59 (17). Ethyl 4,4-dicyano-5-methoxycyclopent-2-(or 3)-enecarboxylate (15) δ[$(CD_3)_2$-CO] 1.36 (3 H, t, $CO_2CH_2$*Me*), 3.06—3.44 (2 H, m, $CH_2$), 3.65—3.90 (1 H, m, $CHCO_2$Et), 3.85 (3 H, s, OMe), 4.35br (2 H, q, $OCH_2$), and 5.42br (1 H, s, C=CH).

(ii) *Complex* (13b). When treated with ammonium ceric nitrate (1.0 g, 1.8 mmol) in methanol (30 ml) as in the above procedure, complex (13b) (152 mg, 0.41 mmol) yielded 5-cyano-2-methoxy-6,6-dimethylhept-2-en-4-one (18) (76 mg, 95%) on elution with ether–light petroleum (1 : 3); $\nu_{max.}$ ($CHCl_3$) 2 230w (C≡N) and 1 678s (C=O, ketone); δ($CDCl_3$) 1.17 (9 H, s, $Bu^t$), 2.33 (3 H, s, Me), 3.21 (1 H, s, CHCN), 3.75 (3 H, s, OMe), and 5.72 (1 H, s, C=CH); *m/e* 195 ($M^+$, 0) 139 (8), 127 (2), 100 (6), 99 (100, $M^+$ — $Bu^t$CHCN), 75 (2), and 59 (3).

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