

Synthesis and oxidation of the decarbonylated adducts generated from alkenes and tricarbonyl(vinylketene)iron(0) complexes

Susan E. Gibson (née Thomas),*^a Stephen P. Saberi,^a Alexandra M. Z. Slawin,^b Paul D. Stanley,^c Mark F. Ward,^a David J. Williams^b and Paul Worthington^c

^a Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

^b Chemical Crystallography Laboratory, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

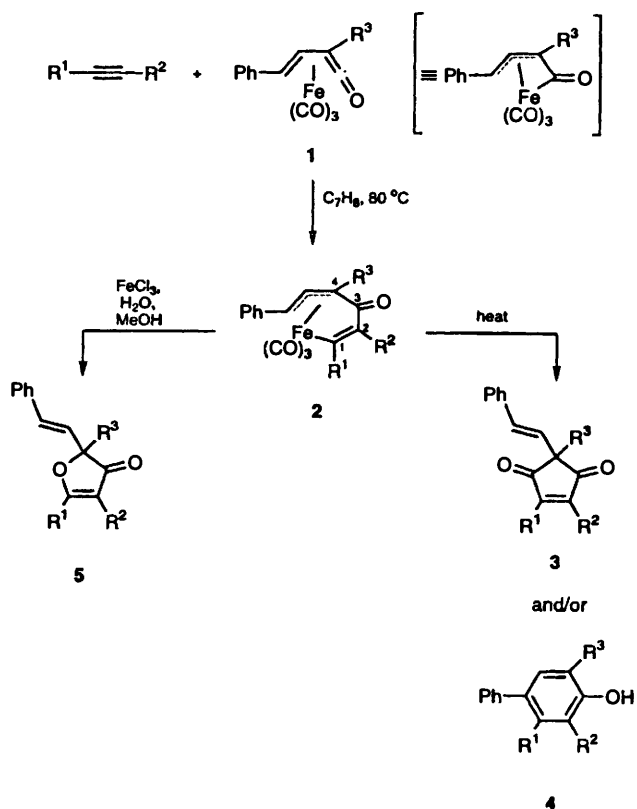
^c Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY, UK

The tricarbonyl(vinylketene)iron(0) complex **6** reacted with dimethyl maleate, dimethyl fumarate, (*E*)-methyl 4-oxopent-2-enoate and (*E*)-ethyl 4,4,4-trifluorobut-2-enoate to give decarbonylated adducts **7–10** respectively. An X-ray crystal structure analysis of the adduct **7**, formed from the complex **6** and dimethyl maleate, and a mechanistic explanation for the formation of the adducts are presented. Oxidation of the adducts **7–10** using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ gave a range of organic products including the tetrasubstituted cyclopropanes **20** and **23–25**, the cyclobutane-1,2-dione **22**, the trisubstituted lactone **21** and the α,β -unsaturated ketone **26**.

The high levels of reactivity exhibited by ketenes and vinylketenes combined with the frequent postulation of metal-bound ketenes and vinylketenes as reaction intermediates,^{1,2} renders the reactivity of isolable metal-bound vinylketenes of considerable interest.^{3,4} We are currently interested in the fundamental reactivity of easily accessible and highly stable iron-centred vinylketene complexes **1** and to date we have reported the results of their reactions with isonitriles,⁵ phosphonoacetate anions,⁶ nucleophiles⁷ and alkynes.^{8–10} Of particular relevance to the work described herein are the reactions of tricarbonyl(vinylketene)iron(0) complexes **1** with alkynes. Alkynes add to these complexes *via* a pathway which is thought to involve dissociation of the styryl group and co-ordination of the alkyne, to generate 1:1 adducts **2** in good yield. Subsequent thermolysis leads to the cyclopentenones **3** and/or the phenols **4** depending on the electronic properties of the C-1 substituent of the adduct,¹⁰ whilst oxidation of the adducts generates furan-3(2*H*)-ones **5**.¹¹ Having discovered that alkynes react smoothly with iron-centred vinylketene complexes to give stable 1:1 adducts and that these adducts afford a range of interesting organic products *via* quite different reaction pathways, it was of interest to us to examine the reactivity of the tricarbonyl(vinylketene)iron(0) complexes **1** towards alkenes. The results of our study, some of which have been published as a communication,¹² are described below. Before embarking upon this study, it was noted that the reactions of tricarbonyl(3,5,5-trimethyl-1-oxapenta-1,2,4-triene)iron(0) with tetracyanoethylene and maleic anhydride had been investigated. These were reported to give an unidentified metal-free 1:1 adduct and an unidentified iron-containing 1:1 adduct, respectively.¹³

Results and discussion

(3-*tert*-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **6** was synthesised by allowing benzylidenemethyl *tert*-butyl ketone to react with $[\text{Fe}_2(\text{CO})_9]$ and treating the resulting tricarbonyliron(0) complex with methyllithium under a carbon monoxide atmosphere according to a literature procedure.⁵ The first alkene to be treated with the yellow–orange crystalline vinylketene complex **6** was the electron-deficient alkene dimethyl maleate. Although no reaction was observed in



toluene at 80°C , the conditions under which a range of alkynes including dimethyl acetylenedicarboxylate had reacted smoothly and rapidly with complex **6** to give 1:1 adducts,¹⁰ a relatively slow reaction was observed when the temperature of the toluene solution of complex **6** and dimethyl maleate was raised to 110°C . Thus, 2 equiv. of dimethyl maleate and complex **6** was heated in toluene under reflux for 3 days under an atmosphere of nitrogen after which the brown turbid product mixture was filtered through a short column of deactivated alumina using diethyl ether as eluent; after this, column chromatography [SiO_2 ; diethyl ether–light petroleum

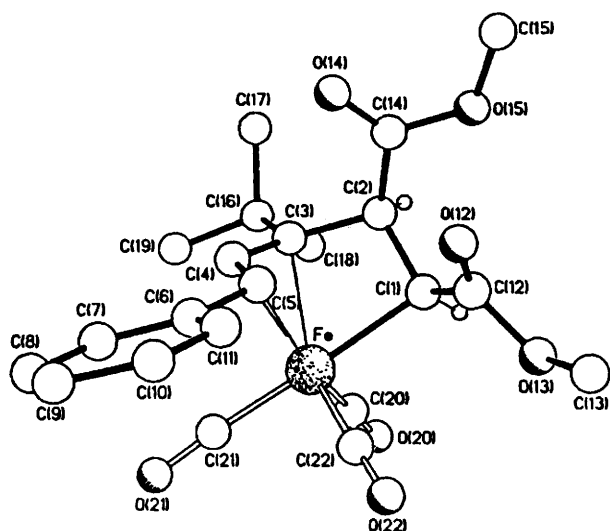


Fig. 1 Molecular structure of the complex **7** ($C_{22}H_{24}O_7Fe$). Selected bond lengths (Å) and bond angles ($^\circ$): Fe–C(1) 2.129(6), C(1)–C(2) 1.527(8), C(2)–C(3) 1.531(8), C(3)–C(4) 1.389(8), C(4)–C(5) 1.414(7), Fe–C(3) 2.242(6), Fe–C(4) 2.107(5) and Fe–C(5) 2.165(5); Fe–C(1)–C(2) 95.4(3), C(1)–C(2)–C(3) 105.8(5), C(2)–C(3)–C(4) 119.3(5), C(3)–C(4)–C(5) 124.1(5) and Fe–C(5)–C(4) 68.5(3).

(bp 40–60 $^\circ C$) 1 : 19 to 1 : 4, gradient elution], and crystallisation gave golden yellow, air-stable crystals (53%). These were identified on the basis of their microanalytical data and their spectroscopic data (IR, 1H NMR, ^{13}C NMR and MS) as a decarbonylated adduct formed from complex **6** and the alkene. The connectivity and relative stereochemistry of the decarbonylated adduct **7** were elucidated by an X-ray crystal structure analysis (Fig. 1).

In order to probe the stereochemistry of this reaction further, complex **6** was allowed to react with dimethyl fumarate under conditions identical with those used in the dimethyl maleate experiment. Work-up gave the adduct **8** (54% yield), the relative stereochemistry of which was determined by X-ray crystallography.¹² It is therefore apparent that the stereochemical integrity of the alkene is maintained during the formation of the decarbonylated adducts.

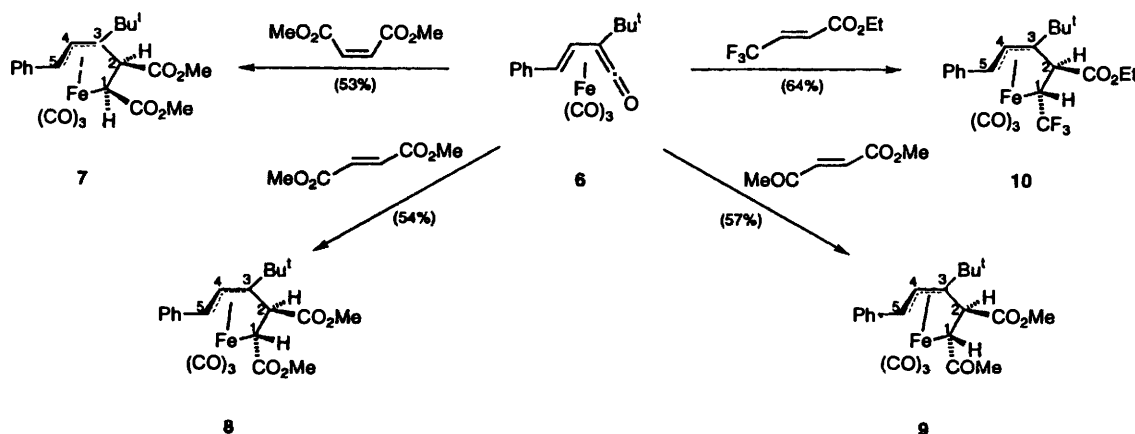
Our attention then turned to other alkenes in order to define the scope of the reaction. We were disappointed to find, however, that the reaction observed with dimethyl maleate and fumarate was not as general as we had hoped for. (It is of note in this context that complex **6** and related complexes react cleanly with a very wide range of alkynes.¹⁰) Thus, styrene, cyclopent-4-ene-1,3-dione, (*E*)-ethyl but-2-enoate, 2-methoxystyrene and diethyl ethylenemalonate all failed to react with complex

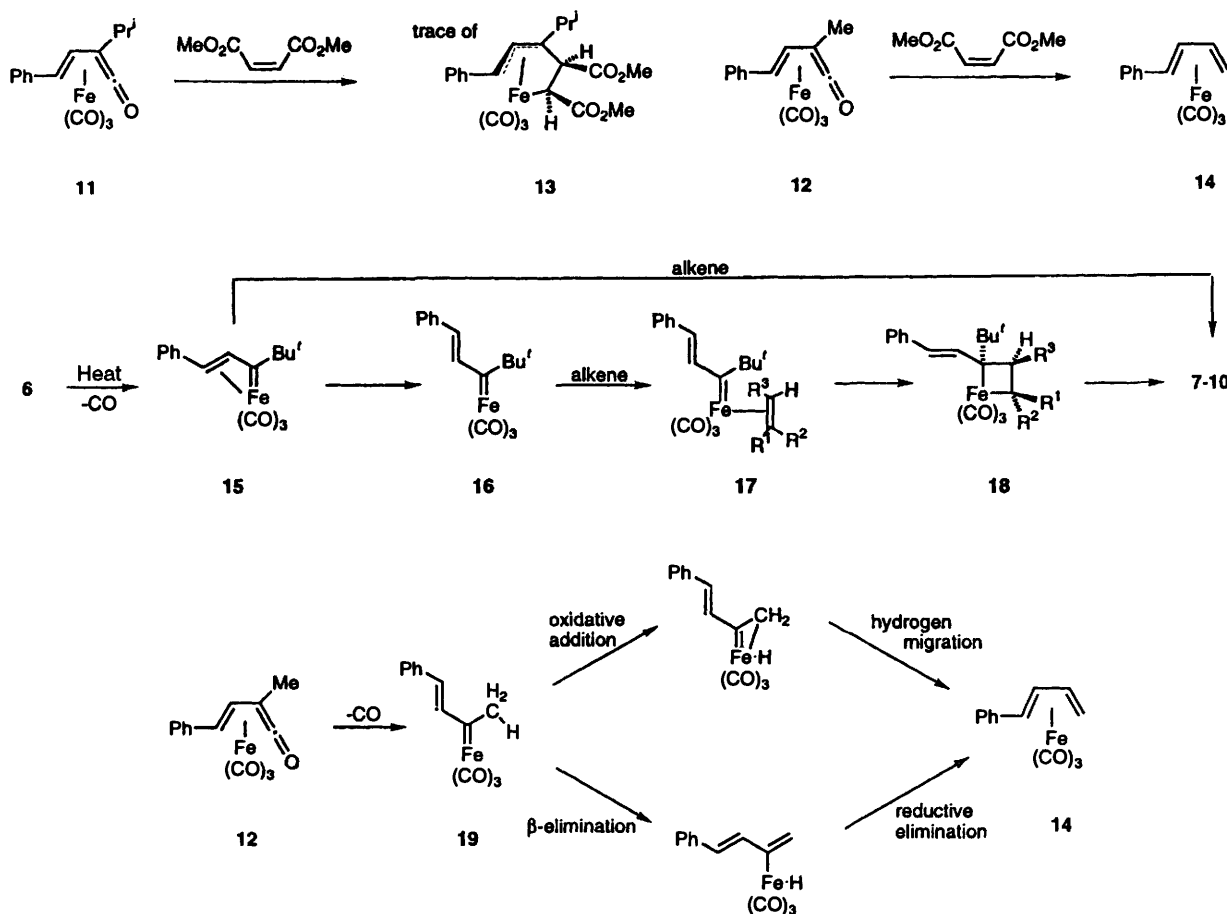
6, even after prolonged heating, whilst methyl acrylate, fumaronitrile, tetracyanoethylene and tetrakis(dimethylamino)ethylene, which did react, gave complex intractable product mixtures.

The regiochemistry of the reaction between vinylketene complexes and alkenes was probed next using (*E*)-methyl 4-oxopent-2-enoate¹⁴ and commercially available (*E*)-ethyl 4,4,4-trifluorobut-2-enoate. Reaction of complex **6** with these alkenes gave the adducts **9** and **10** in 57 and 64% yields respectively. The regiochemistry and relative stereochemistry of **9** and **10** were determined by comparison of their spectroscopic data with those obtained for the adducts **7** and **8** and by NOE and ^{13}C - 1H correlation experiments on the adduct **9**.

Finally, in this part of the investigation, the effect on the reaction of changing the *tert*-butyl group of complex **6** to isopropyl and methyl was examined. Tricarbonyl(3-isopropyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **11** and tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **12** were synthesised according to the published procedure.⁵ The isopropyl substituted complex **11** when allowed to react with dimethyl maleate under conditions identical with those used for the reaction of this alkene with the *tert*-butyl substituted complex **6** gave a complicated mixture of products. Careful chromatography led to the isolation of a trace of material (< 5%) which was tentatively identified as the adduct **13** on the basis of its 1H NMR spectrum. The methyl substituted complex **12** when subjected to the same reaction conditions also gave a mixture of products. Although this product mixture appeared to contain no decarbonylated adduct, it was possible to isolate a complex which was identified as tricarbonyl(1-phenylbuta-1,3-diene)iron(0) **14** by comparison of its 1H NMR, IR and mass spectra with those obtained from an authentic sample of **14** {prepared by heating 1-phenylbuta-1,3-diene with $[Fe_2(CO)_9]$ }.

On the basis of the results described above, the following proposals may be made about the course of the reaction that occurs between vinylketene complex **6** and electron-deficient alkenes. Decarbonylation of **6** gives the η^3 -vinylcarbene intermediate **15** [the interconversion of tricarbonyl(vinylketene)iron(0) complexes and tricarbonyl(η^3 -vinylcarbene)iron(0) complexes has been demonstrated¹⁵]. It is tentatively proposed that this step is rate-determining and requires a temperature greater than 80 $^\circ C$. Formation of the vinylcarbene complex **15** is followed by styryl dissociation to give the 16-electron η^1 -vinylcarbene complex **16**, external alkene coordination to give **17** and a formal [2 + 2] cycloaddition to give the 18-electron ferracyclobutane **18**. This then collapses to the 18-electron products **7**–**10** by recoordination of its styryl double bond. Alternatively, direct interaction between the vinylcarbene complex **15** and the external alkene would lead straight to products **7**–**10**. [Use of enantiomerically pure **6** should





differentiate between these two pathways as the former proceeds *via* a symmetrical intermediate (16) whilst the latter does not.]

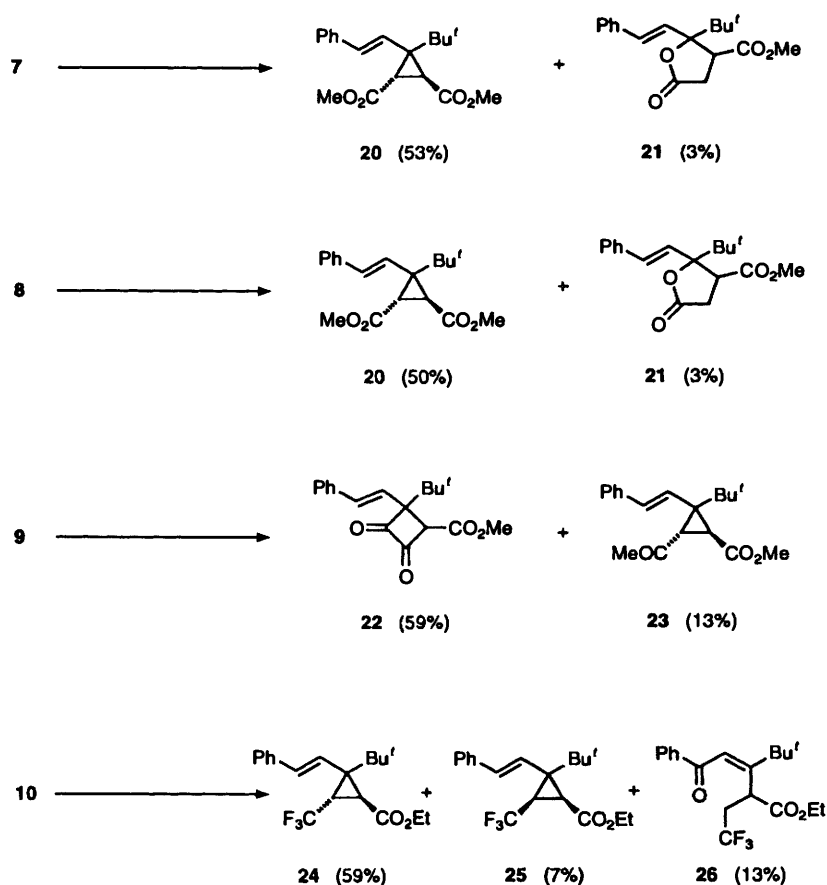
Formation of tricarbonyl(1-phenylbuta-1,3-diene)iron(0) **14** from the vinylketene complex **12** may be accounted for by invoking the formation of the η^2 -carbene **19** followed either by (a) an oxidative addition of the metal into a β carbon-hydrogen bond and a subsequent hydrogen migration, or (b) a β -elimination followed by a reductive elimination/rebinding. Processes of this type may also account for the failure of the reaction between complex **11** and dimethyl maleate to generate appreciable amounts of decarbonylated adduct.

The stereochemical consequences of the reaction are explained by the model described above. Close examination of the stereochemistry of products **7–10** reveals not only that the relative stereochemistry between C-1 and C-2 of the adducts is controlled during the reaction, but also that the relative stereochemistry between C-2 and C-3 is under good control in each reaction. This is consistent with the alkenes approaching either η^1 -carbene complex **16** or η^3 -vinylcarbene complex **15** along a trajectory in which a hydrogen substituent rather than a sterically more demanding methoxycarbonyl or ethoxycarbonyl substituent approaches the *tert*-butyl group of the metal complex. The regiochemical control observed in the formation of adducts **9** and **10** is more difficult to explain. It would appear that the reaction proceeds in a manner which leads to the alkene carbon bearing the substituent most capable of stabilising a build up of negative charge through inductive effects becoming C-1 of the product. This could be interpreted as meaning that the transition state preceding intermediate **18** is a late one and that one of its features is a build up of negative charge on C-1. A similar argument may be applied to the pathway involving direct interaction between complex **15** and the alkenes.

Our next goal was to determine whether or not the tricarbonyliron(0) unit of decarbonylated adducts **7–10** could be removed to leave purely organic products. Thermolysis and photolysis conditions led to very slow and complex reactions but after some experimentation it was discovered that oxidation of these adducts with 10 equiv. of ceric ammonium nitrate in *N,N*-dimethylformamide for 30 min at room temperature gave a relatively fast and clean reaction.

Oxidation of the adducts **7** and **8** (derived from dimethyl maleate and fumarate, respectively) gave identical products. On the basis of their microanalytical and spectroscopic data, the major product from each reaction was identified as the novel tetrasubstituted cyclopropane **20** (53 and 50%, respectively), and the minor product from each reaction was identified as the novel trisubstituted lactone **21** (3% in each case). On the basis of the coupling between the two ring hydrogens of cyclopropane **20** (J 6.8 Hz), the two methoxycarbonyl groups were assigned a *trans* relationship. Thus, oxidation of complexes **7** and **8** leads primarily to a reductive elimination between C-1 and C-3 of the adducts. Sadly, it would appear that stereochemical information about this reductive elimination is lost due to the ease with which the centres bearing the methoxycarbonyl groups can invert. (It is presumed that the cyclopropane isolated is the thermodynamically most stable stereoisomer of this structure.) It is proposed that the lactone **21** is generated by a sequence involving hydrolysis of the C-1 ester group, nucleophilic attack on C-3 and protonation of the organic product.

Oxidation of the adduct **9** [derived from (*E*)-methyl 4-oxopent-2-enoate] also led to the isolation of two products. The major product was identified, somewhat surprisingly, as the cyclobutane-1,2-dione **22** (59%) on the basis of its microanalytical and spectroscopic data, whilst the minor product was identified as the expected tetrasubstituted cyclopropane **23**



Oxidation performed by $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$

(13%). It is currently difficult to define with any certainty how cyclobutane-1,2-dione **22** is formed. It is expected, however, that labelling experiments designed to determine the origin of the carbon atoms in **22**, will clarify the situation.

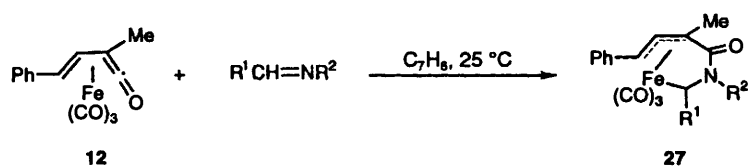
Finally, three organic products were isolated from the oxidation of adduct **10** (derived from (*E*)-ethyl 4,4,4-trifluorobut-2-enoate). These were identified as the trisubstituted cyclopropanes **24** and **25**, 59 and 7% respectively, arising from reductive elimination between C-1 and C-3, and the α,β -unsaturated ketone **26** (13%), which appears to have been formed by reduction of C-1 and oxidation of C-5. On the basis of the coupling constants of the ring hydrogens, the ethoxycarbonyl and trifluoromethyl groups in cyclopropanes **24** and **25** were assigned a *trans* (J 6.9 Hz) and *cis* (J 9.6 Hz) relationship respectively.

In conclusion, it has been demonstrated that tricarbonyl(vinylketene)iron(0) complexes react with electron-deficient alkenes to give decarbonylated adducts and that the tricarbonyliron(0) unit may be removed under oxidative conditions to give predominantly cyclopropanes. It is interesting to compare these results and the results obtained when tricarbonyl(vinylketene)iron(0) complexes were allowed to react with alkynes (outlined in the Introduction), with the reactivity recently reported between tricarbonyl(vinylketene)iron(0) complexes and certain imines.¹⁶ These react at room temperature over 18–24 h to give 1:1 adducts **27** which, on oxidative degradation with $\text{I}_2/\text{Me}_3\text{NO}$, give 2-pyridones or unsaturated δ -lactams, and small amounts of β -lactams. The insertion of the imines into the vinylketene–iron bond probably proceeds *via* yet another different mechanism involving nucleophilic attack of the imine on the electrophilic vinylketene

carbonyl group (which has been shown to be a facile process⁷) and serves to underline the mechanistic diversity and richness of tricarbonyliron(0) complexes of vinylketenes.

Experimental

Reactions under nitrogen and carbon monoxide were performed using standard vacuum line and Schlenk tube techniques.¹⁷ Dry toluene and $[\text{Fe}_2(\text{CO})_9]$ were bought from Aldrich Chemical Company. *N,N*-Dimethylformamide (DMF) was dried over molecular sieves. Unless stated otherwise reagents were obtained from Aldrich Chemical Company. (3-*tert*-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **6**,⁵ tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **12**,⁵ (*E*)-methyl 4-oxopent-2-enoate,¹⁴ 1-phenylbuta-1,3-diene¹⁸ and tricarbonyl(1-phenylbuta-1,3-diene)iron(0)¹⁹ were prepared according to literature methods. Melting points, which are uncorrected, were determined using an Electrothermal IA9100 Digital or a Gallenkamp capillary melting point apparatus at Imperial College or a Mettler FP62 melting point apparatus at Zeneca Agrochemicals. The mps of organoiron complexes were measured in sealed capillaries under nitrogen. IR spectra were obtained on a Perkin-Elmer 1710 or Mattson 5000 FTIR spectrometer instrument at Imperial College or a Perkin-Elmer 268 IR spectrophotometer at Zeneca Agrochemicals. NMR spectra were recorded at room temperature on JEOL GSX 270 (270 MHz ^1H , 67.9 MHz ^{13}C) and Bruker DRX 300 (75.5 MHz ^{13}C) spectrometers at Imperial College or a JEOL GSX 270 (270 MHz ^1H , 254.1 MHz ^{19}F , 67.9 MHz ^{13}C) spectrometer at Zeneca Agrochemicals. J Values are given in H_2 . Mass spectra were recorded on a VG Micromass 7070E

**Table 1** ^1H NMR (δ_{H})^a data for adducts

Complex	1-H	2-H	Bu ^t	4-H	5-H	Phenyl	Others
7	1.78 (d, <i>J</i> 12.2)	3.74 (d, <i>J</i> 12.2)	1.25 (s)	5.67 (d, <i>J</i> 12.2)	5.15 (d, <i>J</i> 12.2)	7.24–7.43 (m)	3.62 (3 H, s, CO ₂ CH ₃) 3.65 (3 H, s, CO ₂ CH ₃)
8	0.94 (d, <i>J</i> 6.5)	4.52 (d, <i>J</i> 6.5)	1.35 (s)	5.50 (d, <i>J</i> 11.9)	3.93 (d, <i>J</i> 11.9)	7.31–7.46 (m)	3.60 (3 H, s, CO ₂ CH ₃) 3.74 (3 H, s, CO ₂ CH ₃)
9	1.18 (d, <i>J</i> 6.8)	4.74 (d, <i>J</i> 6.8)	1.36 (s)	5.57 (d, <i>J</i> 11.8)	4.05 (d, <i>J</i> 11.8)	7.28–7.49 (m)	2.17 (3 H, s, COCH ₃) 3.58 (3 H, s, CO ₂ CH ₃)
10	0.62–0.78 (m)	3.78 (d, <i>J</i> 7.5)	1.27 (s)	5.35 (d, <i>J</i> 11.9)	3.92 (d, <i>J</i> 11.9)	7.15–7.38 (m)	1.15 (3 H, t, <i>J</i> 7.1, CH ₂ CH ₃) 3.97–4.06 (2 H, m, CH ₂ CH ₃)

^a CDCl₃, 300 K, 270 MHz.**Table 2** ^{13}C - $\{^1\text{H}\}$ NMR (δ_{C})^a data for adducts

Complex	C-1	C-2	C-3	C-4	C-5	Metal carbonyls	Phenyl	Others
7	-4.2	42.7	84.0	92.1	68.9	205.4 210.9 211.6	126.0 (C _{o/m}) 127.3 (C _p) 129.0 (C _{o/m}) 140.0 (C _{ipso})	29.7 [C(CH ₃) ₃] 36.9 [C(CH ₃) ₃] 51.0 (CO ₂ CH ₃) 51.8 (CO ₂ CH ₃) 170.7 (CO ₂ Me) 179.3 (CO ₂ Me)
8	6.1	43.6	87.6	91.8	71.6	204.4 210.4 210.5	125.1 (C _{o/m}) 127.4 (C _p) 129.1 (C _{o/m}) 139.6 (C _{ipso})	30.5 [C(CH ₃) ₃] 36.5 [C(CH ₃) ₃] 51.7 (CO ₂ CH ₃) 52.0 (CO ₂ CH ₃) 173.0 (CO ₂ Me) 180.5 (CO ₂ Me)
9	17.6	41.7	81.8	92.3	71.7	210.0 210.4 212.4	126.0 (C _{o/m}) 127.6 (C _p) 129.2 (C _{o/m}) 139.2 (C _{ipso})	28.1 (COCH ₃) 30.6 [C(CH ₃) ₃] 36.9 [C(CH ₃) ₃] 52.0 (CO ₂ CH ₃) 173.3 (CO ₂ Me) 204.4 (COMe)
10	7.7 (q, <i>J</i> _{CF} 30)	43.7 (q, <i>J</i> _{CF} 5)	86.2	91.3	71.7	204.0 (q, <i>J</i> _{CF} 2) 209.9 (q, <i>J</i> _{CF} 2) 210.3	125.9 (C _{o/m}) 127.5 (C _p) 129.1 (C _{o/m}) 139.4 (C _{ipso})	14.0 (CH ₂ CH ₃) 30.6 [C(CH ₃) ₃] 36.5 [C(CH ₃) ₃] 61.3 (CH ₂ CH ₃) 131.6 (q, <i>J</i> _{CH} 275, CF ₃) 172.1 (CO ₂ Et)

^a CDCl₃, 300 K, 67.9 MHz.

instrument or a Kratos MS890MS at Imperial College and a JEOL JMS DX300 instrument at Zeneca Agrochemicals.

Reaction of dimethyl maleate and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6

(3-*tert*-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6 (340 mg, 1.00 mmol) and dimethyl maleate (288 mg, 2.00 mmol) were dissolved in dry toluene (25 cm³). The resultant yellow solution was thoroughly degassed and heated to reflux under a small positive pressure of nitrogen for 72 h. The reaction mixture was allowed to cool after which the brown turbid mixture was filtered through a short pad of alumina (Brockman, Grade IV), eluting with diethyl ether. Removal of the solvent from the filtrate under reduced pressure gave a yellow solid. Chromatography [SiO₂; diethyl ether–light petroleum (bp 40–60 °C), 5:95 to 20:80, gradient elution] followed by recrystallisation from dichloromethane–light petroleum (bp

60–80 °C) gave (3,4,5- η)-[3-*tert*-butyl-1,2-di(methoxycarbonyl)-5-phenylpent-3-enyl]tricarbonyliron(0) 7 as golden yellow crystals (242 mg, 0.53 mmol, 53%), mp 155–156 °C (decomp.) (Found: C, 57.8; H, 5.3. C₂₂H₂₄FeO₇ requires C, 57.91; H, 5.30%); ν_{max} (CCl₄/cm⁻¹) 2058vs, 2000vs and 1985vs (C≡O); *m/z* (FAB, NOBA) 457 (MH⁺, 31%). See Tables 1 and 2 for ^1H and ^{13}C NMR spectroscopic data.

Reaction of dimethyl fumarate and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6

Complex 6 (340 mg, 1.00 mmol) and dimethyl fumarate (288 mg, 2.00 mmol) were dissolved in dry toluene (50 cm³). The resultant yellow solution was thoroughly degassed and refluxed under a positive pressure of nitrogen for 72 h. The reaction mixture was allowed to cool after which the brown turbid mixture was filtered through a short pad of alumina (Brockman, Grade IV), eluting with diethyl ether. Removal of

the solvent from the filtrate under reduced pressure gave a yellow solid. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 5:95 to 20:80, gradient elution] followed by recrystallisation from dichloromethane–light petroleum (bp 60–80 °C) gave (3,4,5- η)-[3-*tert*-butyl-1,2-di(methoxycarbonyl)-5-phenylpent-3-enyl]tricarbonyliron(0) **8** as golden yellow crystals (246 mg, 0.54 mmol, 54%), mp 150–152 °C (decomp.) (Found: C, 57.9; H, 5.2. $\text{C}_{22}\text{H}_{24}\text{FeO}_7$ requires C, 57.91; H, 5.30%); $\nu_{\text{max}}(\text{CCl}_4/\text{cm}^{-1})$ 2062vs, 2006vs and 1990vs ($\text{C}\equiv\text{O}$); m/z (FAB, NOBA) 913 ($[\text{2M} + \text{H}]^+$, 4%) and 457 (MH^+ , 5%). See Tables 1 and 2 for ^1H and ^{13}C NMR spectroscopic data.

Reaction of (*E*)-methyl 4-oxopent-2-enoate and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **6**

Complex **6** (340 mg, 1.00 mmol) and (*E*)-methyl 4-oxopent-2-enoate (257 mg, 2.00 mmol) were dissolved in dry toluene (25 cm^3). The resultant yellow solution was thoroughly degassed and refluxed under a positive pressure of nitrogen for 60 h. The reaction mixture was allowed to cool after which the brown turbid mixture was filtered through a short pad of alumina (Brockman, Grade IV), eluting with diethyl ether. Removal of the solvent from the filtrate under reduced pressure gave a yellow solid. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 10:90] followed by recrystallisation from dichloromethane–light petroleum (bp 60–80 °C) gave (3,4,5- η)-[1-*acetyl*-3-*tert*-butyl-2-methoxycarbonyl-5-phenylpent-3-enyl]tricarbonyliron(0) **9** as golden yellow crystals (238 mg, 0.57 mmol, 57%), mp 163–164 °C (decomp.) (Found: m/z , 463.0832. $\text{C}_{22}\text{H}_{24}\text{O}_6\text{FeNa}$ requires 463.0919); $\nu_{\text{max}}(\text{cyclohexane}/\text{cm}^{-1})$ 2040vs and 1980vs ($\text{C}\equiv\text{O}$); m/z (FAB, NOBA) 441 (MH^+ , 38%). See Tables 1 and 2 for ^1H and ^{13}C NMR spectroscopic data.

Reaction of (*E*)-ethyl 4,4,4-trifluorotert-2-enoate and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **6**

Complex **6** (340 mg, 1.00 mmol) and (*E*)-ethyl 4,4,4-trifluorobut-2-enoate (336 mg, 2.00 mmol) were dissolved in dry toluene (25 cm^3). The resultant yellow solution was thoroughly degassed and refluxed under a positive pressure of nitrogen for 30 h. (*E*)-Ethyl 4,4,4-trifluorobut-2-enoate (336 mg, 2.00 mmol) was added and the reaction mixture was heated for a further 42 h. The reaction mixture was allowed to cool after which the brown turbid mixture was filtered through a short pad of alumina (Brockman, Grade IV), eluting with diethyl ether. Removal of the solvent from the filtrate under reduced pressure gave a yellow solid. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 1:199 to 5:95, gradient elution] followed by recrystallisation from dichloromethane–light petroleum (bp 60–80 °C) gave (3,4,5- η)-[3-*tert*-butyl-2-methoxycarbonyl-5-phenyl-1-(trifluoromethyl)pent-3-enyl]tricarbonyliron(0) **10** as yellow crystals (307 mg, 0.64 mmol, 64%), mp 112–113 °C (decomp.) (Found: C, 55.2; H, 4.8. $\text{C}_{22}\text{H}_{23}\text{F}_3\text{FeO}_5$ requires C, 55.0; H, 4.8%); $\nu_{\text{max}}(\text{cyclohexane}/\text{cm}^{-1})$ 2060vs, 2000vs and 1995vs ($\text{C}\equiv\text{O}$); δ_{F} (254.05 MHz, CDCl_3 , CFCl_3) –60.6 (3 F, s, CF_3); m/z (FAB, NOBA) 481 (MH^+ , 8%). See Tables 1 and 2 for ^1H and ^{13}C NMR spectroscopic data.

Assignment of the regiochemistry and stereochemistry of adducts **9 and **10****

The regiochemistry and relative stereochemistry of the adducts **9** and **10** were determined by comparison of their spectroscopic data with those obtained for the adducts **7** and **8**, and by NOE and ^{13}C - ^1H correlation experiments of adduct **9**. Thus a *trans* relationship was assigned to 1-H and 2-H in the adducts **9** and **10** by comparison of the magnitude of their coupling constants (J 6.8 and 7.5 Hz respectively) with those of the fumarate-

derived adduct **8** (J 6.5 Hz) and the maleate-derived adduct **7** (J 12.2 Hz). The relative stereochemistry between C-2 and C-3 in the complexes **9** and **10** was assigned as illustrated, on the basis of a better correlation between their δ_{H} values for 1-H, 2-H, 4-H and 5-H and the corresponding δ_{H} values for adduct **8** than for adduct **7**. Irradiation of the protons of the Bu^t group in adduct **9** strongly enhanced the signals at δ_{H} 4.74 (32%) and 5.57 (30%) thus confirming their assignments as 2-H and 4-H respectively.

The regiochemistry of adduct **10** follows from its fluorine coupling. The regiochemistry of adduct **9** was determined as follows. The ^1H -coupled ^{13}C spectrum of **9** revealed that the resonances at δ_{C} 17.6 and 41.7 originated from CCOMe and CCO_2Me respectively on the basis that long-range proton coupling was observed at δ_{C} 17.6 and not at δ_{C} 41.7. $^{13}\text{C}/^1\text{H}$ correlation spectroscopy then revealed a one-bond coupling between 2-H (δ_{H} 4.74) and CCO_2Me and a two-bond coupling between 2-H and CCOMe thus fixing the regiochemistry as illustrated.

Reaction of dimethyl maleate and tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **12**

Complex **12** (298 mg, 1.00 mmol) and dimethyl maleate (288 mg, 2.00 mmol) were dissolved in dry toluene (25 cm^3). The resultant yellow solution was thoroughly degassed and refluxed under a positive pressure of nitrogen for 72 h. The reaction mixture was allowed to cool after which the brown turbid mixture was filtered through a short pad of alumina (Brockman, Grade IV), eluting with diethyl ether. Removal of the solvent from the filtrate under reduced pressure gave a yellow solid. Chromatography [SiO_2 ; light petroleum (bp 40–60 °C)] gave tricarbonyl(1-phenylbuta-1,3-diene)iron(0) **14** as an oily orange–yellow solid (32 mg, 0.12 mmol, 12%) the TLC, IR, MS and ^1H NMR spectra of which agreed with those of an authentic sample (see below).

Preparation of tricarbonyl(1-phenylbuta-1,3-diene)iron(0) **14¹⁹**

1-Phenylbuta-1,3-diene (1.11 g, 8.5 mmol) and nonacarbonyl-diiron (4.66 g, 12.8 mmol) were refluxed in hexane under nitrogen for 2.5 h. The resultant cloudy green mixture was filtered through a short pad of Kieselguhr. Chromatography [AlO_3 (neutral, Brockman I); light petroleum (bp 40–60 °C)] followed by recrystallisation from light petroleum (bp 40–60 °C) gave the desired product **14** as orange–yellow crystals (1.77 g, 6.6 mmol, 77%); mp 61–62 °C (lit.,²⁰ 59–61 °C) (Found: C, 57.8; H, 3.8. $\text{C}_{13}\text{H}_{10}\text{FeO}_3$ requires C, 57.82; H, 3.73%); $\nu_{\text{max}}(\text{CCl}_4/\text{cm}^{-1})$ 2049vs and 1989vs ($\text{C}\equiv\text{O}$); δ_{H} (270 MHz; CDCl_3 ; CHCl_3) 0.65 (1 H, ddd, J 9.4, 2.7 and 1.0, *cis*- CH_2CH), 1.89 (1 H, ddd, J 7.4, 2.7 and 1.0, *trans*- CH_2CH), 2.06 (1 H, d, J 9.4 CHCHPh), 5.44–5.35 (1 H, m, PhCHCH), 5.92 (1 H, dd, J 9.4 and 5.0, CH_2CH) and 7.16–7.32 (5 H, m, Ph); δ_{C} (67.9 MHz, CDCl_3 , CHCl_3) 39.6 (CH_2CH), 61.5 (CHCHPh), 81.3 (CH_2CH), 83.5 (PhCHCH), 126.1 ($\text{C}_{o/m}$), 128.3 (C_p), 128.5 ($\text{C}_{o/m}$), 140.6 (C_{ipso}) and 211.3 (3 \times CO); m/z (CI, NH_3) 271 (MH^+ , 67%) and 131 ($\text{MH}^+ - \text{Fe}(\text{CO})_3$, 100%).

Oxidative decomplexation of adduct **7 formed from dimethyl maleate and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **6****

The adduct **7** (228 mg, 0.50 mmol) was dissolved in dry DMF (20 cm^3). Addition of ammonium cerium(IV) nitrate (1.37 g, 2.50 mmol) to the solution with stirring, resulted in effervescence. The initially dark red solution became orange after 15 min, and a further portion of ammonium cerium(IV) nitrate (1.37 g, 2.50 mmol) was added to it. After a further 15 min all the starting material had disappeared, as judged by TLC [Kieselgel 60F₂₅₄, light petroleum (bp 40–60 °C)–diethyl ether, 3:1]. Dichloromethane (50 cm^3) was added to the reaction

mixture which was then extracted with water. The aqueous extract was washed with dichloromethane ($2 \times 50 \text{ cm}^3$). The combined organic layers were washed with brine, dried (MgSO_4) and the solvents removed from the mixture under reduced pressure to yield a brown oil. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 2:98 to 1:4, gradient elution] followed by recrystallisation from diethyl ether–light petroleum (bp 40–60 °C) yielded *dimethyl 3-tert-butyl-3-styrylcyclopropane-r-1,t-2-dicarboxylate* **20** (84 mg, 0.27 mmol, 53%) as white feathery crystals, mp 137–139 °C (decomp.) (Found: C, 71.8; H, 7.7. $\text{C}_{19}\text{H}_{24}\text{O}_4$ requires C, 72.13; H, 7.65%); ν_{max} ($\text{KBr}/\text{cm}^{-1}$) 1737vs and 1723vs (ester C=O); δ_{H} (270 MHz; CDCl_3 ; CHCl_3) 1.00 [9 H, s, $\text{C}(\text{CH}_3)_3$], 2.64 (1 H, d, J 6.8, CHCO_2Me), 2.71 (1 H, d, J 6.8, CHCO_2Me), 3.64 (3 H, s, CO_2CH_3), 3.74 (3 H, s, CO_2CH_3), 6.18 (1 H, d, J 15.9, PhCHCH), 6.58 (1 H, d, J 15.9, PhCHCH) and 7.21–7.33 (5 H, m, Ph); δ_{C} (67.9 MHz; CDCl_3 ; CHCl_3) 27.3 (CHCO_2Me), 28.0 [$\text{C}(\text{CH}_3)_3$], 32.4 (CHCO_2Me), 35.0 [$\text{C}(\text{CH}_3)_3$], 46.9 [$\text{CC}(\text{CH}_3)_3$], 51.9 (CO_2Me), 52.1 (CO_2Me), 126.3 (C_{Oim}), 127.5 ($\text{C}_{\text{p/PhCHCH}}$), 127.8 ($\text{C}_{\text{p/PhCHCH}}$), 128.8 (C_{Oim}), 134.7 (PhCHCH), 136.7 (C_{ipso}), 170.1 (CO_2Me) and 170.3 (CO_2Me); m/z (CI, NH_3) 334 (MNH_4^+ , 12%), 314 (MH^+ , 71%).

Methyl 2-tert-butyl-5-oxo-2-styrylfuran-3-carboxylate **21** (4 mg, 0.01 mmol, 3%) was isolated as a light brown oil by chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 1:99 to 1:9, gradient elution] from the residues of the previous column (Found: m/z 303.1604. $\text{C}_{18}\text{H}_{22}\text{O}_4$ requires 303.1596); ν_{max} (cm^{-1}) 1783vs (lactone C=O) and 1739vs (ester C=O); δ_{H} (270 MHz; CDCl_3 ; CHCl_3) 1.08 [9 H, s, $\text{C}(\text{CH}_3)_3$], 2.73 (1 H, dd, J 9.9 and 18.2, CHHCO_2R), 3.13 (1 H, dd, J 6.9 and 18.2, CHHCO), 3.60 (1 H, dd, CHCO_2Me), 3.66 (1 H, s, CO_2CH_3), 6.25 (1 H, d, J 16.1, PhCHCH), 6.70 (1 H, d, J 16.1, PhCHCH) and 7.27–7.34 (5 H, m, Ph); δ_{C} (67.9 MHz; CDCl_3 ; CHCl_3) 25.1 [$\text{C}(\text{CH}_3)_3$], 32.6 [$\text{C}(\text{CH}_3)_3$], 39.2 [$\text{CC}(\text{CH}_3)_3$], 45.2 (CH_2CO_2), 52.4 (CO_2Me), 92.5 (CHCO_2Me), 124.6 (PhCHCH), 126.5 (C_{Oim}), 128.0 (PhCHCH), 128.7 (C_{Oim}), 131.1 (C_{p}), 136.2 (C_{ipso}), 171.0 (CO_2Me), 174.7 (CO_2R); m/z (CI, NH_3) 334 (MNH_4^+ , 72%), 314 (MH^+ , 100%).

Oxidative decomplexation of adduct 8 formed from dimethyl fumarate and (3-tert-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6

The adduct **8** (228 mg, 0.50 mmol) was dissolved in dry DMF (20 cm^3). Addition of ammonium cerium(IV) nitrate (1.37 g, 2.50 mmol), with stirring, resulted in effervescence. The initially dark red solution became orange after 15 min, and a further portion of ammonium cerium(IV) nitrate (1.37 g, 2.50 mmol) was added to it. After a further 15 min all the starting material had disappeared, as judged by TLC [Kieselgel 60F₂₅₄ light petroleum (bp 40–60 °C)–diethyl ether, 3:1]. Dichloromethane (50 cm^3) was added to the reaction mixture which was then extracted with water. The aqueous extract was washed with dichloromethane ($2 \times 50 \text{ cm}^3$). The combined organic layers were washed with brine, dried (MgSO_4) and the solvents removed from the mixture under reduced pressure to yield a brown oil. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 2:98 to 1:4, gradient elution] followed by recrystallisation from diethyl ether–light petroleum (bp 40–60 °C) yielded cyclopropane **20** (79 mg, 0.25 mmol, 50%) as white feathery crystals. The IR, ^1H and ^{13}C NMR spectral data of these crystals were identical with those obtained from an authentic sample (see above).

The lactone **21** (5 mg, 0.02 mmol, 3%) was isolated as a light brown oil by chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 1:99 to 1:9, gradient elution] from the residues of the previous column; its IR, ^1H and ^{13}C NMR spectral data were identical with those obtained from an authentic sample (see above).

Oxidative decomplexation of adduct 9 formed from (E)-methyl-4-oxopent-2-enoate and (3-tert-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6

The adduct **9** (55 mg, 0.125 mmol) was dissolved in dry DMF (10 cm^3). Addition of ammonium cerium(IV) nitrate (343 mg, 0.626 mmol), with stirring, resulted in effervescence. The initially dark red solution became orange, after 15 min, and a further portion of ammonium cerium(IV) nitrate (343 mg, 0.626 mmol) was added to it. After a further 15 min all the starting material had disappeared, as judged by TLC [Kieselgel 60F₂₅₄ light petroleum (bp 40–60 °C)–diethyl ether, 3:1]. Dichloromethane (20 cm^3) was added to the reaction mixture which was then extracted with water. The aqueous extract was washed with dichloromethane ($2 \times 20 \text{ cm}^3$). The combined organic layers were washed with brine, dried (MgSO_4) and the solvents removed from the mixture under reduced pressure to yield a brown oil. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 1:19 to 1:4, gradient elution] gave *methyl 2-tert-butyl-3,4-oxo-2-styrylcyclobutane-1-carboxylate* **22** (22 mg, 0.73 mmol, 59%) as a very pale yellow solid, mp 86–88 °C (Found: m/z 301.1436. $\text{C}_{18}\text{H}_{21}\text{O}_4$ requires 301.1440); ν_{max} ($\text{Nujol}/\text{cm}^{-1}$) 1752vs (ester C=O) and 1730vs (1,2-dicarbonyl C=O); δ_{H} (270 MHz; CDCl_3 ; CHCl_3) 1.05 [9 H, s, $\text{C}(\text{CH}_3)_3$], 3.90 (1 H, s, CO_2CH_3), 6.51 (1 H, s, CHCO_2CH_3), 6.78 (1 H, d, J 16.1, PhCHCH), 6.92 (1 H, d, J 16.1, PhCHCH) and 7.26–7.43 (5 H, m, Ph); δ_{C} (67.9 MHz; CDCl_3 ; CHCl_3) 25.9 [$\text{C}(\text{CH}_3)_3$], 39.5 [$\text{C}(\text{CH}_3)_3$], 52.9 (CO_2CH_3), 95.7 [$\text{CC}(\text{CH}_3)_3$], 123.8 (CHCO_2CH_3), 125.6 (PhCHCH), 126.8 (C_{Oim}), 128.1 ($\text{C}_{\text{p/PhCHCH}}$), 128.6 (C_{Oim}), 130.6 ($\text{C}_{\text{p/PhCHCH}}$), 136.1 (C_{ipso}), 159.8 (C=O), 162.7 (C=O) and 170.2 (CO_2Me); m/z (CI, NH_3) 318 (MNH_4^+ , 81%), 301 (MH^+ , 68%).

Methyl t-3-acetyl-2-tert-butyl-2-styrylcyclopropane-r-1-carboxylate **23** (5 mg, 0.02 mmol, 13%) was isolated as a colourless solid by preparative thin layer chromatography [Kieselgel 60F₂₅₄, light petroleum (bp 40–60 °C)–diethyl ether, 2:1] from the residues of the previous column (Found: m/z 301.1825. $\text{C}_{19}\text{H}_{25}\text{O}_3$ requires 301.1804); ν_{max} ($\text{Nujol}/\text{cm}^{-1}$) 1735vs (ester C=O) and 1708vs (ketone C=O); δ_{H} (270 MHz; CDCl_3 ; CHCl_3) 1.00 [9 H, s, $\text{C}(\text{CH}_3)_3$], 2.44 (1 H, s, COCH_3), 2.78 (1 H, d, J 7.1, CHCO_2Me), 2.83 (1 H, d, J 7.1, CHCOMe), 3.65 (1 H, s, CO_2CH_3), 6.23 (1 H, d, J 15.7, PhCHCH), 6.58 (1 H, d, J 15.7, PhCHCH) and 7.23–7.38 (5 H, m, Ph); δ_{C} (67.9 MHz; CDCl_3 ; CHCl_3) 27.7 (CHCO_2Me), 28.7 [$\text{C}(\text{CH}_3)_3$], 29.1 (COCH_3), 35.8 [$\text{C}(\text{CH}_3)_3$], 41.4 ($\text{CC}(\text{CH}_3)_3$), 50.0 (CHCOMe), 51.9 (CO_2CH_3), 126.4 (C_{Oim}), 127.7 (PhCHCH), 128.6 ($\text{C}_{\text{Oim/PhCHCH}}$), 128.7 ($\text{C}_{\text{Oim/PhCHCH}}$), 134.3 (C_{p}), 136.8 (C_{ipso}), 170.3 (CO_2Me), 203.6 (COMe); m/z (CI, NH_3) 318 (MNH_4^+ , 44%), 301 (MH^+ , 81%).

Oxidative decomplexation of adduct 10 formed from (E)-ethyl 4,4,4-trifluoro but-2-enoate and (3-tert-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 6

The adduct **10** (480 mg, 1.00 mmol) was dissolved in dry DMF (20 cm^3). Addition of ammonium cerium(IV) nitrate (2.74 g, 5.00 mmol) to the solution, with stirring, resulted in effervescence. The initially dark red solution became orange, after 15 min, and a further portion of ammonium cerium(IV) nitrate (2.74 g, 5.00 mmol) was added to it. After a further 15 min all the starting material had disappeared, as judged by TLC [Kieselgel 60F₂₅₄, light petroleum (bp 40–60 °C)–diethyl ether, 3:1]. Dichloromethane (20 cm^3) was added to the reaction mixture which was then extracted with water. The aqueous extract was washed with dichloromethane ($2 \times 20 \text{ cm}^3$). The combined organic layers were washed with brine, dried (MgSO_4) and the solvents removed from the mixture under reduced pressure to yield a yellow oil. Chromatography [SiO_2 ; diethyl ether–light petroleum (bp 40–60 °C), 1:39 to 1:9, gradient elution] followed by recrystallisation from diethyl

ether–light petroleum (bp 40–60 °C) yielded *ethyl 2-tert-butyl-2-styryl-t-3-(trifluoromethyl)cyclopropane-r-1-carboxylate* **24** (181 mg, 0.26 mmol, 59%) as a colourless solid, mp 71–72 °C (decomp.) (Found: C, 66.8; H, 6.6. C₁₉H₂₃F₃O₂ requires C, 67.05; H, 6.81%); ν_{\max} (Nujol/cm⁻¹) 1732vs (ester C=O); δ_{H} [270 MHz; Si(CH₃)₄, CHCl₃] 1.09 [9 H, s, C(CH₃)₃], 2.21 (1 H, t, *J* 7.2, CO₂CH₂CH₃), 2.52–2.66 (2 H, m, ³*J*_{HCC} 6.9 and ³*J*_{FCC} 10.3, CHCO₂Me + CHCF₃), 4.07–4.19 (2 H, m, CO₂CH₂CH₃), 6.15 (1 H, d, *J* 15.7, PhCHCH), 6.50 (1 H, d, *J* 15.7, PhCHCH) and 7.21–7.34 (5 H, m, Ph); δ_{F} (254.05 MHz; CDCl₃; CFCl₃) –54.9 (3 F, s, CF₃); δ_{C} (67.9 MHz; CDCl₃, CHCl₃) 14.2 (CO₂CH₂CH₃), 26.8 [C(CH₃)₃], 28.2 q, *J* 2, CC(CH₃)₃, 32.8 q, *J* 39, (CCF₃), 34.4 [C(CH₃)₃], 45.8 (q, *J* 2, CCO₂CH₂CH₃), 61.1 (CO₂CH₂CH₃), 125.8 q, *J* 273, CF₃), 126.3 (C_o), 127.8 (C_p/PhCHCH), 128.3 (C_p/PhCHCH), 128.6 (C_m), 135.1 (C_{ipso}), 136.4 (PhCHCH) and 168.8 (CO₂Et); *m/z* (CI, NH₃) 358 (MNH₄⁺, 100%), 341 (MH⁺, 96%).

Ethyl 2-tert-butyl-2-styryl-c-3-(trifluoromethyl)cyclopropane-r-1-carboxylate **25** (23 mg, 0.07 mmol, 7%) was isolated as a yellow oil (Found: *m/z* 341.1728. C₁₉H₂₄O₂F₃ requires 341.1728); ν_{\max} (cm⁻¹) 1744vs (ester C=O); δ_{H} (270 MHz; CDCl₃; CHCl₃) 0.98 [9 H, s, C(CH₃)₃], 1.23 (1 H, t, *J* 7.1, CO₂CH₂CH₃), 1.95 (1 H, dq, *J* 1.2 and 9.6, CHCF₃), 2.25 (1 H, d, *J* 9.6, CHCO₂Et), 3.65 (1 H, q, *J* 7.2, CO₂CH₂CH₃), 6.38 (1 H, dq, *J* 1.7 and 16.5, PhCHCH), 6.54 (1 H, d, *J* 16.5, PhCHCH) and 7.23–7.38 (5 H, m, Ph); δ_{F} (254.05 MHz; CDCl₃, CFCl₃) –56.3 (3 F, s, CF₃); *m/z* (CI, NH₃) 358 (MNH₄⁺, 100%), 341 (MH⁺, 34%).

(Z)-ethyl 3-tert-butyl-6,6,6-trifluoro-1-oxo-1-phenylhex-2-ene-4-carboxylate **26** (47 mg, 0.13 mmol, 13%) was isolated as a yellow oil (Found: *m/z* 357.1698. C₁₉H₂₄F₃O₃ requires 357.1678); ν_{\max} (CCl₄/cm⁻¹) 1740vs (ester C=O) and 1665vs (PhC=O); δ_{H} (270 MHz; CDCl₃; CHCl₃) 1.14 (3 H, t, *J* 7.1, CO₂CH₂CH₃), 1.28 [9 H, s, C(CH₃)₃], 2.16–2.24 (1 H, m, CHCO₂Et), 3.52–3.65 (2 H, m, CH₂CF₃), 4.01–4.10 (1 H, m, CO₂CH₂CH₃), 6.97 (1 H, s, PhCOCH) and 7.42–7.91 (5 H, m, Ph); δ_{F} (254.05 MHz; CDCl₃; CFCl₃) –64.71 (3 F, t, *J* 9.8, CF₃); δ_{C} (67.9 MHz; CDCl₃; CHCl₃) 14.1 (CO₂CH₂CH₃), 28.9 [C(CH₃)₃], 36.3 (q, *J*_{CF} 29, CH₂CF₃), 39.3 [C(CH₃)₃], 39.5 (q, *J*_{CF} 3, CHCH₂CF₃), 61.3 (COCH₂CH₃), 120.0 (PhCOCH), 126.7 (q, *J*_{CF} 277, CF₃), 128.2(C_{oim}), 128.6 (C_{oim}) 132.9 (C_p), 138.9 (C_{ipso}), 164.8 [CC(CH₃)₃], 170.4 (CO₂Et) and 191.4 (PhCO); *m/z* (CI, NH₃) 374 (MNH₄⁺, 10%), 357 (MH⁺, 100%), 299 (MNH₄⁺ – CF₃, 11%), 282 (MH⁺, 3%).

X-Ray crystallographic analysis of 7

Crystal data. Single crystals of **7**, suitable for X-ray crystallography were grown from dichloromethane–light petroleum (bp 60–80 °C). C₂₂H₂₄FeO₇, *M* = 456.3, orthorhombic, *a* = 12.966(5), *b* = 17.674(7), *c* = 9.710(5) Å, *V* = 2225(2) Å³, space group *Pna*2₁, *Z* = 4, *D*_c = 1.362 g cm⁻³, Mo radiation, λ = 0.710 73 Å, μ (Mo-K α) = 7.1 cm⁻¹, *F*(000) = 952, crystal dimensions 0.23 × 0.26 × 0.33 mm. Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Mo-K α radiation using ω scans. 2072 Independent reflections ($2\theta < 50^\circ$) were measured and of these 1667 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors but not for absorption. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of all the hydrogen atoms were revealed in a ΔF map. These positions were idealised C–H = 0.96 Å, the atoms assigned isotropic thermal parameters $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and allowed to ride on their parent carbon atoms. Refinement was by full-

matrix least squares to give *R* = 0.0375, *R*_w = 0.0385 [$w^{-1} = \sigma^2(F) + 0.0008F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.38 and –0.24 e Å⁻³. The polarity of the structure was determined by the refinement of a free variable η which multiplies all f'' ; this parameter was refined to a value of 0.95(14) providing a definitive assignment. Computations were carried out on a 486 PC using the SHELXTL-PC program system.²¹ Atomic coordinates, bond lengths, angles and thermal parameters have been deposited with the Cambridge Crystallographic Centre.

Acknowledgements

The authors thank Mr James A. Stern for a generous gift of (*E*)-methyl 4-oxopent-2-enoate, Zeneca Agrochemicals for a CASE Award (MFW), the EPSRC for a post-doctoral fellowship (SPS), Zeneca Fine Chemicals Businesses for the 1993 Zeneca Award in Organic Chemistry and the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Science.

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Paper 5/01980J

Received 29th March 1995

Accepted 15th May 1995