

Iron(III)Chloride Oxidation of Tricarbonyl(vinylketene)iron(0)-Alkyne Adducts

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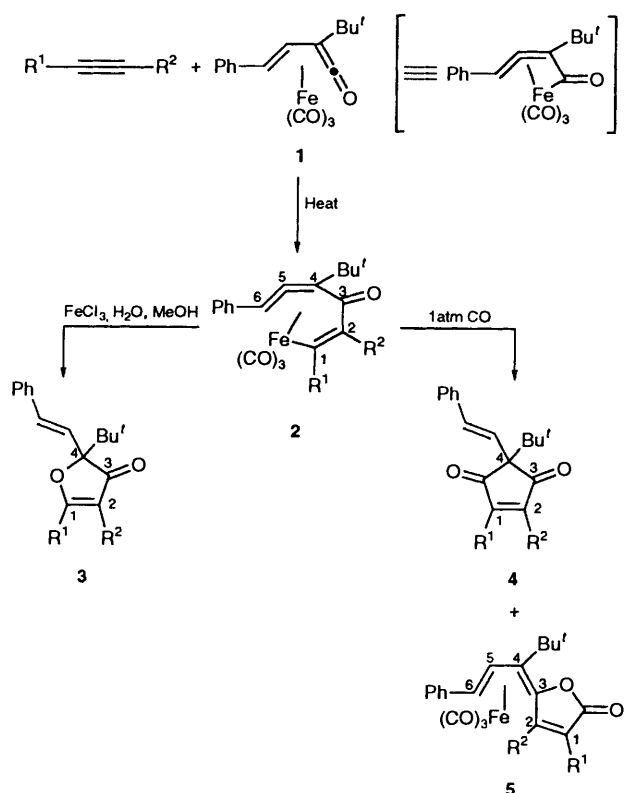
Oxidation of the adducts formed from tricarbonyl(vinylketene)iron(0) complexes and alkynes by iron(III) chloride in methanol/water leads to the replacement of the tricarbonyliron(0) unit with an oxygen atom derived from the water. This pathway to furan-3(2*H*)-ones requires the presence of an electron-withdrawing substituent on carbon-2 of the vinylketene-alkyne adduct. Data used to assign the structures of some of the vinylketene-alkyne adducts used in this study included an X-ray crystal structure analysis of the unusual lactone complex **5c**.

We are currently interested in the fundamental reactivity of easily accessible and highly stable iron-centred vinylketene complexes such as complex **1**, and we have reported the results of their reactions with isonitriles,¹ phosphonoacetate anions² and a range of nucleophiles.³ More recently we have examined their reactivity towards alkynes and found that they add to tricarbonyl(vinylketene)iron(0) complexes to give the stable adducts **2**.^{4,5} In order to compare the reactivity of our organoiron system with related organo-chromium and -cobalt systems, we subsequently examined thermolytic methods of generating organic products from the adducts **2**.^{6,5} Thermolysis of the adducts led to either cyclopent-2-ene-1,4-diones or phenols and its outcome was found to be dependent on the nature of the substituent on C-1 of the adduct.^{6,5} In this paper, we describe a novel method of removing the organic ligand from adducts **2**, in which the tricarbonyliron(0) unit is replaced by an oxygen atom to give furan-3(2*H*)-ones **3**. Carbonylation of the vinylketene-alkyne adducts generated during this study was also undertaken and the outcome of these experiments is also described.

Results and Discussion

The adduct **2a** ($R^1 = R^2 = \text{CO}_2\text{Me}$) was synthesised in 80–85% yield by heating together dimethyl acetylenedicarboxylate and the vinylketene complex **1** at 80 °C.⁵ Attempts to generate organic products by thermolysis of the adduct **2a** met with little success. Thus, thermolysis of **2a** at 72 °C for 166 h led to the recovery of starting material in 69% yield (see Table 1); at 90 °C for 17 h it led to an essentially intractable mixture of organic and inorganic materials;⁵ and in the presence of triphenylphosphine (76 °C, 7 days) it gave the corresponding cyclopent-2-ene-1,4-dione **4a** in only 22% yield.⁵ In an attempt to facilitate the elimination of the tricarbonyliron(0) unit from adduct **2a**, the latter was treated with iron(III) chloride in methanol–water at 63 °C for 2.5–3 h. Work-up of the product mixture gave the substituted furan-3(2*H*)-one **3a** as white crystals, identified on the basis of IR, ¹H NMR, ¹³C NMR, low and high resolution mass spectral results and microanalytical data. Thus, under the reaction conditions described, the tricarbonyliron(0) unit in **2a** is cleanly replaced by an oxygen atom to give **3a** in 70% yield (see Table 1).

This unusual oxygen 'insertion' reaction was investigated further by treating several other vinylketene-alkyne adducts with iron(III) chloride. Initially, the previously reported adduct **2b** ($R^1 = \text{CO}_2\text{Me}$, $R^2 = \text{H}$) was examined.^{4,5} [It is of note that the regiochemistry of this adduct had been determined



earlier by comparison of its ¹H and ¹³C NMR data with those obtained from a closely related complex ($R^1 = \text{Ac}$, $R^2 = \text{H}$) which had been analysed by X-ray crystallography.⁴] Treatment of the adduct **2b** with FeCl_3 for 3 h at 63 °C gave a crude product which contained no signals corresponding to those expected for the desired oxidised product and subsequent chromatography led to the isolation of starting material in 70% yield. Thus, it was postulated that an electron-withdrawing group on C-2 of the adduct was a necessary structural feature for oxygen 'insertion' to occur. Adduct **2b** also failed to produce any cyclopent-2-ene-1,4-dione when heated for 49 h at 72 °C under a carbon monoxide atmosphere.

Since our previous studies had revealed that addition of monosubstituted alkynes to tricarbonyl(vinylketene)iron(0) complexes gave adducts in which the alkyne substituent was located on C-1 of the resulting adduct,⁵ it now seemed necessary to examine how previously neglected unsymmetrical

Table 1 Oxidation^a and carbonylation^b of the vinylketene-alkyne adducts **2a–e**

Entry	R ¹	R ²	Adduct	Oxidation ^a			Carbonylation ^b				
				Time (h)	Product	Yield (%)	Time (h)	Product	Yield (%)	Product	Yield (%)
1	CO ₂ Me	CO ₂ Me	2a	2.5–3	3a	70	166	4a	— ^c	5a	—
2	CO ₂ Me	H	2b	3	3b	— ^d	49	4b	— ^e	5b	—
3	Ph	CO ₂ Et	2c	5	3c	55	50	4c^f	52	5c	15
4	Ph	SO ₂ Me	2d	5	3d	80	23	4d	55	5d	17
5	SO ₂ Me	Ph	2e	95	3e	—	22	4d	—	5e	—

^a FeCl₃ (50 equiv.), H₂O, MeOH, 63 °C. ^b 1 atm CO, C₇H₈, 72 °C. ^c Starting material **2a** recovered in 69% yield. ^d Starting material **2b** recovered in 70% yield. ^e Starting material **2b** recovered in 48% yield. ^f R¹ = Ph, R² = CO₂Me.

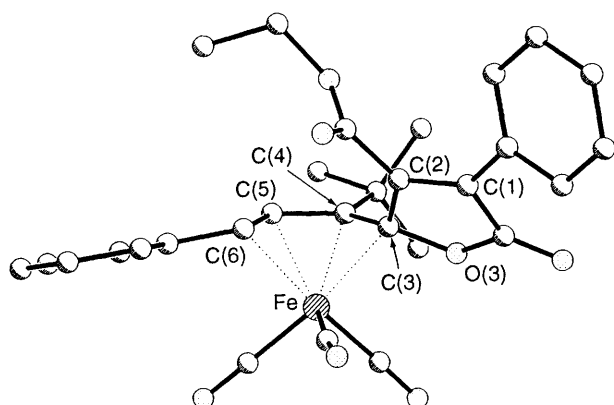
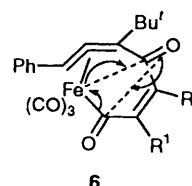


Fig. 1 Molecular structure of the complex **5c** (C₂₉H₂₆FeO₇). Selected bond lengths (Å) and bond angles(°): C(2)–C(3) 1.484(6), C(3)–C(4) 1.442(7), C(4)–C(5) 1.406(6), C(5)–C(6) 1.417(6), C(3)–O(3) 1.423(6), Fe–C(3) 2.080(5), Fe–C(4) 2.083(5), Fe–C(5) 2.074(5) and Fe–C(6) 2.135(5); C(2)–C(3)–C(4) 127.7(4), C(2)–C(3)–O(3) 103.7(4), C(3)–C(4)–C(5) 114.9(4) and C(4)–C(5)–C(6) 122.9(4).

disubstituted alkynes would interact with vinylketene complexes in order to synthesise more adducts with an electron-withdrawing substituent on C-2. Thus, the vinylketene complex **1** was treated with ethyl phenylpropiolate and methyl phenylethynyl sulphone.

The reaction between the vinylketene complex **1** and ethyl phenylpropiolate gave a single adduct in moderate yield (45%), the regiochemistry of which could not be assigned unambiguously from its spectroscopic data. It was, nevertheless, oxidised with iron(III) chloride in methanol–water for 5 h at 63 °C to give, on work-up, the furan-3(2*H*)-one **3c** (R¹ = Ph, R² = CO₂Me) as colourless crystals. The regiochemistry of **3c** was determined by comparing its ¹³C NMR values for C-1 and C-2 with calculated values for the two possible regioisomers. Thus, R¹ and R² of the adduct **2c** which produced **3c** were assigned as Ph and CO₂Et respectively (note that transesterification of the ethoxycarbonyl group of the adducts occurs under the reaction conditions). Adduct **2c** was also heated under a carbon monoxide atmosphere at 72 °C for 50 h and chromatography of the product mixture gave not only cyclopent-2-ene-1,4-dione **4c** in reasonable yield (52%), but also a second product which was identified by X-ray crystallography as the unexpected lactone complex **5c** (see Fig. 1). [Inspection of the bonding around C-3 in complex **5c** reveals an extreme case of the rotation of *exo* and *endo* substituents normally observed in tricarbonyl(η⁴-diene)-iron(0) complexes and an η³-allyl-η¹-allyl representation of its structure may be more appropriate.] It is postulated that the first step in the formation of **5c** is insertion of carbon monoxide into the iron–carbon-1 bond of adduct **2c** to give **6c**, a process very closely related to a step in the mechanism proposed for a recently reported conversion of alkyne(cyclopentadiene)iron

complexes into trisubstituted 4,6a-dihydropentalen-1(3*aH*)-ones.⁷ Product **5c** may then be formed by the six-electron process indicated on structure **6**. The carbon connectivity of **5c** provided further support for the regiochemical assignment of adduct **2c**.



The two possible regioisomers of the product adduct were isolated from the reaction between the vinylketene complex **1** and methyl phenylethynyl sulphone and their reactivity proved to be dramatically different. The more polar isomer was readily oxidised to a furan-3(2*H*)-one (5 h, 63 °C; 80%) and carbonylated to the cyclopent-2-ene-1,4-dione **4d** (23 h, 72 °C; 55%), whilst the less polar isomer was only slowly and uncleanly oxidised [95 h, 63 °C; ¹H NMR spectrum of crude product contained resonances for starting material and the corresponding furan-3(2*H*)-one in a 2:1 ratio together with evidence for substantial decomposition] and proved resistant to carbonylation (22 h, 72 °C; ¹H NMR spectrum of crude product contained only resonances corresponding to starting material). Substituents R¹ and R² of the furan-3(2*H*)-one produced from the more polar isomer were assigned as Ph and SO₂Me, respectively, by comparison of the ¹³C NMR spectroscopic data for the furanone with calculated values. Hence, the more polar and more reactive vinylketene–alkyne adduct was designated **2d** (R¹ = Ph, R² = SO₂Me) and the less polar and less reactive vinylketene–alkyne adduct was designated **2e** (R¹ = SO₂Me, R² = Ph).

In order to determine the origin of the oxygen atom which replaces the tricarbonyliron(0) fragment when vinylketene–alkyne adducts **2** are heated with iron(III) chloride in methanol–water, the reaction of the adduct **2a** was repeated using 95 atom% H₂¹⁸O. The furan-3(2*H*)-one **3a** was isolated in 56% yield and analysed by mass spectrometry. The ratio of peaks at *m/z* 361 [M(¹⁸O)H] and 359 [M(¹⁶O)H] was found to be 1.27. This was compared with the value of 0.15 measured for the ratio of the same peaks in the spectrum obtained from the sample prepared in the presence of H₂¹⁶O. Thus, it appears that the 'inserted' oxygen in this reaction is derived from water. Hence, it is postulated from this result and from the observation that electron-withdrawing substituents on C-2 facilitate the oxygen 'insertion' process, that the oxygen–carbon-1 bond of the furan-3(2*H*)-one is created by nucleophilic attack of a water-derived oxygen nucleophile on C-1 of the vinylketene–alkyne adduct. The process by which the second oxygen–carbon bond is formed is as yet unclear.

Experimental

Reactions under nitrogen and carbon monoxide were performed according to standard vacuum line and Schlenk tube techniques.⁸ Tetrahydrofuran was distilled from sodium benzophenone ketyl. Toluene was dried over Na wire. Methanol was dried by refluxing with Mg/I₂ followed by distillation under nitrogen and storage over activated 4Å sieves. Light petroleum (LP) was distilled prior to use and refers to the fraction boiling in the range 40–60 °C. Enneacarbonyliron,⁹ tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **1**,¹ and the adducts it forms with dimethyl acetylenedicarboxylate **2a**⁵ and methyl propiolate **2b**⁵ were prepared according to published procedures. The concentration of BuLi was determined by titration against diphenylacetic acid.¹⁰ All other reagents were used as obtained from commercial sources. M.p.s were obtained using a Reichert 7905 microscope hot stage or a Gallenkamp capillary m.p. apparatus and are uncorrected. Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department and Imperial College Micro-analytical Service. IR spectra were recorded using a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded in CDCl₃ on JEOL GSX 270 (270 MHz, ¹H) and Bruker AM500 (125.8 MHz, ¹³C) spectrometers; *J* values are given in Hz. Mass spectra were recorded on a VG Micromass 7070E instrument at Imperial College and on VG Mass Lab 12/250 and VG Analytical ZAB/E instruments at the SERC Mass Spectrometry Service Centre, Swansea using CI, EI and FAB (matrix-*m*-nitrobenzyl alcohol and thioglycerol) techniques.

Reaction of (3-tert-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 1 with Ethyl Phenylpropiolate.—(3-*tert*-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **1** (680 mg, 2.00 mmol) and ethyl phenylpropiolate (348 mm³, 2.00 mmol) were dissolved in dry nitrogen-saturated toluene (20 cm³) in a Schlenk tube and heated at 42 °C for 90 h under a nitrogen atmosphere. The reaction mixture was allowed to cool and the solvent removed under reduced pressure. The resulting dark brown residue was dissolved in diethyl ether and the solution filtered through a short column of alumina (Brockmann 1, neutral; diethyl ether) to give a dark brown–yellow solution which upon evaporation gave a brown–yellow residue. This was washed with cold light petroleum to yield a light yellow microcrystalline solid which was washed with more cold light petroleum (5 × 20 cm³) to afford the pure microcrystalline canary yellow adduct **2c** (450 mg, 45%). Upon recrystallisation from degassed CH₂Cl₂–LP this gave a bright yellow crystalline solid, m.p. 117–119 °C [Found: C, 65.1; H, 4.9. C₂₈H₂₆FeO₆ requires C, 65.38; H, 5.10%; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2070m (C=O), 2014m (C=O), 1718w (CO₂Et) and 1653w (C=O); δ_{H} 0.83 (3 H, t, *J* 4, CO₂CH₂CH₃), 1.58 [9 H, s, C(CH₃)₃], 3.88 (2 H, m, CO₂CH₂CH₃), 4.36 (1 H, d, *J* 12, PhCH=CH), 5.81 (1 H, d, *J* 12, PhCH=CH) and 7.1–7.4 (10 H, m, 2 × Ph); δ_{C} 13.7 (CH₂CH₃), 32.2 [C(CH₃)₃], 38.2 [C(CH₃)₃], 60.5 (CH₂CH₃), 79.4 (C-6), 90.4 (C-5), 114.6 (C-4), 122.3 (C_{ortho}/C_{meta}), 126.0 (C_{ortho}/C_{meta}), 127.1 (C_{para}), 128.3 (C_{ortho}/C_{meta}), 128.4 (C_{para}), 129.4 (C_{ortho}/C_{meta}), 137.5 (C_{ipso}), 147.4, 150.7 (C-2 and C_{ipso}), 163.7 (CO₂Et), 194.7, 204.6, 206.8, 209.7 and 210.8 (C-1, C-3 and 3 × C=O); *m/z* (FAB, MNBA + CH₂Cl₂) 515 (MH⁺, 13%), 487 (MH – CO, 36), 459 (MH – 2CO, 7) and 431 (MH – 3CO, 100).

Synthesis of Methyl Phenylethynyl Sulphone.—Phenylacetylene (1.11 cm³, 10 mmol) in dry THF (20 cm³) was cooled to –78 °C and then BuLi (2.3 mol dm⁻³; 4.5 ml, 10.35 mmol) was added dropwise to it *via* a syringe over 1 min. The lemon yellow solution was stirred at –78 °C for 1 h and then methane-sulfonyl chloride (0.785 ml, 10.2 mmol) was added dropwise to the mixture *via* a syringe causing a slight darkening of the

solution. The reaction mixture was allowed to warm to room temperature when saturated aqueous ammonium chloride (25 cm³) was added to it. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 30 cm³). The combined organic phases were washed with water (2 × 25 cm³) and brine (25 ml) and dried (MgSO₄), filtered and evaporated under reduced pressure to give pure title compound as a fluffy cream solid (1.08 g, 60%); this was recrystallised from CH₂Cl₂–LP to give cream needles, m.p. 50–52 °C [Found: *m/z* 198.0589. C₉H₁₂NSO₂ (M + NH₄) requires 198.0588]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2186m (C≡C), 1330m (SO₂) and 1152m (SO₂); δ_{H} 2.46 (3 H, s, SO₂CH₃) and 7.34–7.58 (5 H, m, Ph); δ_{C} 46.8 (SO₂CH₃), 84.4 (C≡CSO₂Me) 91.5 (C≡CSO₂Me), 117.4 (C_{ipso}), 128.8 (C_{ortho}/C_{meta}), 131.7 (C_{para}) and 132.8 (C_{ortho}/C_{meta}); *m/z* (EI) 180 (M⁺, 36%) 165 (M – CH₃, 9) and 89 (C≡CSO₂, 100).

Reaction of (3-tert-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) 1 with Methyl Phenylethynyl Sulphone.—(3-*tert*-Butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0) **1** (510 mg, 1.50 mmol) and methyl phenylethynyl sulfone (270 mg, 1.50 mmol) were dissolved in dry degassed toluene (25 cm³), and the solution heated at 42 °C for 65 h. It was then filtered through alumina as described above in the synthesis of adduct **2c** and evaporated. The bright yellow residue was triturated several times with diethyl ether to remove non-organometallic impurities and the solid residue was subjected to flash column chromatography (SiO₂; LP–Et₂O, 10:1 graduated to 1:1; sample pre-adsorbed onto SiO₂). This gave adducts **2d** (*R*_f 0.12; 0.2 mm Kieselgel 60 GF₂₅₄; LP–Et₂O, 4:1) (200 mg, 26%) and **2e** (*R*_f 0.63; 0.2 mm Kieselgel 60 GF₂₅₄; LP–Et₂O, 4:1) (350 mg, 45%) as bright yellow microcrystalline solids which were recrystallised from CH₂Cl₂–LP.

Data for **2d**: m.p. 155–158 °C [Found: *m/z* 521.0741. C₂₆H₂₅FeO₆S (MH) requires 521.0721]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2075m (C=O), 2025m (C=O) and 1661vw [C(3)=O]; δ_{H} 1.53 [9 H, s, C(CH₃)₃], 2.99 (3 H, s, SO₂CH₃), 4.24 (1 H, d, *J* 13, PhCH=CH), 5.83 (1 H, d, *J* 13, PhCH=CH) and 7.3–7.5 (5 H, m, Ph); δ_{C} 32.0 [C(CH₃)₃], 38.2 [C(CH₃)₃], 42.8 (SO₂CH₃), 79.1 (C-6), 89.7 (C-5), 112.2 (C-4), 120.2 (v, br) (C_{ortho}/C_{meta}), 126.0 (C_{ortho}/C_{meta}), 127.3 (C_{para}), 128.2 (v, br) (C_{ortho}/C_{meta}), 128.9 (C_{para}), 129.6 (C_{ortho}/C_{meta}), 136.7 (C_{ipso}), 146.4, 150.6 (C_{ipso} and C-2), 194.0, 204.1, 204.7, 209.0 and 225.0 (C-1, C-3 and 3 × C=O); *m/z* (FAB, NOBA) 521 (MH⁺, 51%), 493 (MH – CO, 83), 437 (M – 3CO, 100) and 357 (M – 3CO – SO₂Me, 78).

Data for **2e**: m.p. 183–187 °C [Found: *m/z* 521.0721; C₂₆H₂₅FeO₆S (MH) requires 521.0721]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2080m (C=O), 2030m (C=O) and 1666vw [C(3)=O]; δ_{H} 1.51 [9 H, s, C(CH₃)₃], 2.30 (3 H, s, SO₂CH₃), 4.17 (1 H, d, *J* 13, PhCH=CH), 5.90 (1 H, d, *J* 13, PhCH=CH) and 7.35–7.5 (5 H, m, Ph); δ_{C} 32.1 [C(CH₃)₃], 38.3 [C(CH₃)₃], 43.4 (SO₂CH₃), 81.0 (C-6), 89.5 (C-5), 112.3 (C-4), 126.3, 128.6, 128.8, 129.1, 129.5, 129.6, 136.5, 136.6 (2 × Ph), 153.6 (C-2), 198.7, 199.2 (C-1 and C-3), 205.3, 206.1 and 207.0 (3 × C=O); *m/z* (FAB, NOBA) 521 (MH⁺, 90%), 493 (MH – CO, 7), 464 (M – 2CO, 25), 437 (M – 3CO, 100) and 357 (M – 3CO – SO₂Me, 38).

Oxidation of the Adduct 2a.—The adduct **2a** (96.4 mg, 200 μmol) and iron(III) chloride (1.6 g, ~50 equiv.) were placed in a dry Schlenk tube and dry methanol (8 cm³) and distilled water (72 mm³, 4.00 mmol) were cautiously added to them under a nitrogen atmosphere (exothermic dissolution). The mixture was then carefully degassed and heated at 63 °C for 2.5–3 h, by which time TLC analysis indicated that the reaction was complete. Water (5–10 cm³) was added to the cooled reaction mixture (room temp.) with vigorous stirring and then it was poured into a separating funnel containing diethyl ether (25

cm³). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 25 cm³). The combined organic layers were then washed with distilled water (25 cm³) and saturated brine (25 cm³), dried (MgSO₄) and evaporated under reduced pressure to give a brown residue. This was chromatographed (SiO₂; LP-Et₂O, 4:1) to afford a white powdery solid (50 mg, 70%) which was recrystallised from LP-Et₂O to give the furan-3(2*H*)-one **3a** as white crystals, m.p. 111–113 °C (Found: C, 67.0; H, 6.2. C₂₀H₂₂O₆ requires C, 67.03; H 6.19%) [Found: *m/z* 359.1499. C₂₀H₂₃O₆ (MH) requires 359.1495]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1751s (ring C=O), 1719m (CO₂Me) and 1613m (C=C); δ_{H} 1.10 [9 H, s, C(CH₃)₃], 3.82 (3 H, s, CO₂CH₃), 4.03 (3 H, s, CO₂CH₃), 6.28 (1 H, d, *J* 16, PhCH=CH), 6.71 (1 H, d, *J* 16, PhCH=CH) and 7.25–7.4 (5 H, m, Ph); δ_{C} 24.2 [C(CH₃)₃], 39.4 [C(CH₃)₃], 52.2, 53.7 (2 × CO₂CH₃), 99.8 (C-4), 110.9 (C-2), 121.4 (PhCH=CH), 126.8 (C_{ortho}/C_{meta}), 128.4 (C_{ortho}/C_{meta}), 128.6 (C_{para}), 132.6 (PhCH=CH), 135.5 (C_{ipso}), 159.9, 161.0 (2 × CO₂CH₃), 178.1 (C-1) and 196.7 (C-3); *m/z* (FAB, thioglycerol 359 (MH⁺, 59%), 302 (M – isobutene, 82), 285 (M – isobutene – Me) and 142 [OCC(CO₂H)=C(CO₂H), 100].

Oxidation of the Adduct 2b.—The adduct **2b** (43 mg, 100 μmol) was treated with iron(III) chloride (800 mg, ~50 equiv.) in methanol (4 cm³) and water (36 mm³, 2.00 mmol) for 3 h at 63 °C according to the method given above for adduct **2a**. This gave a brown oily residue, the ¹H NMR spectrum of which contained no signals corresponding to those expected for the desired oxidised product but only those of the starting material plus evidence of some decomposition. Flash column chromatography (SiO₂; LP-Et₂O, 4:1) of the residue gave a yellow solid (30 mg, 70%) whose ¹H NMR spectrum was identical with that of the starting material.

Oxidation of the Adduct 2c.—The adduct **2c** (154 mg, 300 μmol) was treated with iron(III) chloride (2.4 g, ~50 equiv.) in methanol (12 cm³) and water (108 mm³, 6.00 mmol) for 5 h at 63 °C according to the method given above for the adduct **2a**. Work-up gave a brown oily residue which, after flash column chromatography (SiO₂; LP-Et₂O, 9:1) and subsequent crystallisation yielded the furan-3(2*H*)-one **3c** as fine colourless crystals (65 mg, 55%), m.p. 153–155 °C [Found: *m/z* 377.1753. C₂₄H₂₅O₄ (MH) requires 377.1752]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1771vs (ring C=O), 1730m (CO₂Me) and 1640w (C=C); δ_{H} 0.93 [9 H, s, C(CH₃)₃], 3.69 (3 H, s, CO₂CH₃), 6.72 (1 H, d, *J* 16, PhCH=CH), 6.93 (1 H, d, *J* 16, PhCH=CH) and 7.3–7.5 (10 H, m, 2 × Ph); δ_{C} 25.5 [C(CH₃)₃], 39.8 [C(CH₃)₃], 52.3 (CO₂CH₃), 65.8 (C-4), 94.2 (C-2), 121.5 (PhCH=CH), 126.8 (C_{ortho}/C_{meta}), 127.3 (C_{ortho}/C_{meta}), 128.5 (C_{para}), 128.6 (C_{ortho}/C_{meta}), 128.9 (C_{ortho}/C_{meta}), 129.9 (C_{para}), 132.6 (PhCH=CH), 132.6 (C_{ipso}), 136.0 (C_{ipso}), 161.7 (CO₂CH₃), 167.7 (C-1) and 174.8 (C-3); *m/z* (CI) 377 (MH⁺, 38%) and 333 (100).

Oxidation of the Adduct 2d.—The adduct **2d** (52 mg, 100 μmol) was treated with iron(III) chloride (800 mg, ~50 equiv.) in dry methanol (4 cm³) and water (36 mm³, 2.00 mmol) at 63 °C for 5 h according to the method described above for adduct **2a**. Work-up gave a brown–green residue which was chromatographed (SiO₂; LP-Et₂O, 9:1) to yield the furan-3(2*H*)-one **3d** as a viscous semi-solid oil (32 mg, 80%) [Found: *m/z* 414.1739. C₂₃H₂₈NSO₄ (M + NH₄) requires 414.1739]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1763mw (ring C=O) and 1620w (C=C); δ_{H} 0.94 [9 H, s, C(CH₃)₃], 3.23 (3 H, s, SO₂CH₃), 6.69 (1 H, d, *J* 16, PhCH=CH), 6.92 (1 H, d, *J* 16, PhCH=CH) and 7.35–7.5 (10 H, m, 2 × Ph); δ_{C} 25.4 [C(CH₃)₃], 40.4 [C(CH₃)₃], 42.7 (SO₂CH₃), 65.8 (C-4), 95.1 (C-2), 120.2 (PhCH=CH), 126.8 (Ph), 127.7 (Ph), 128.5 (Ph), 128.8 (Ph), 129.0 (Ph), 130.5 (C_{ipso}), 130.7 (Ph), 132.6 (PhCH=CH), 135.6 (C_{ipso}), 165.9 (C-1) and

175.9 (C-3); *m/z* (EI) 397 (MH⁺, 2%) and 340 (M – isobutene, 100).

Oxidation of the Adduct 2e.—The adduct **2e** (108 mg, 204 μmol) was treated with iron(III) chloride (1.64 g, ~50 equiv.) in methanol (7.5 cm³) and water (72 mm³, 4.00 mmol) at 63 °C for 95 h according to the method given above for adduct **2a**. Work-up gave a black–brown residue, the ¹H NMR of which contained signals corresponding to those of the desired oxidised product and of the starting material **2e** (~1:2) together with evidence for substantial decomposition. Isolation of either pure **2e** or pure oxidised product proved impossible because of the large number of by-products.

Carbonylation of the Adduct 2a.—The adduct **2a** (48 mg, 100 μmol) was heated under a carbon monoxide atmosphere in toluene (5 cm³) at 72 °C for 166 h as described below for the adduct **2c**. Filtration through a short plug of alumina gave a yellow–brown residue whose ¹H NMR spectrum contained none of the resonances expected for the desired cyclopentenedione but only those of the starting material and those due to decomposition. Flash column chromatography (SiO₂; LP-Et₂O, 1:1) yielded the adduct **2a** (33 mg, 69%) as a lemon yellow microcrystalline solid which was identified by comparison of its ¹H NMR spectrum with that of an authentic sample.

Carbonylation of the Adduct 2b.—The adduct **2b** (21 mg, 50 μmol) was heated under a carbon monoxide atmosphere in toluene (2 cm³) at 72 °C for 49 h as described below for the adduct **2c**. Filtration through a short plug of alumina gave a yellow–brown residue whose ¹H NMR spectrum contained none of the resonances expected for the desired cyclopentenedione but only those of the starting material and those due to two unidentifiable compounds. Flash column chromatography (SiO₂; LP-Et₂O, 1:1) yielded the adduct **2b** (10 mg, 48%) as a pale yellow microcrystalline solid which was identified by comparison of its ¹H NMR spectrum with that of an authentic sample.

Carbonylation of the Adduct 2c.—The adduct **2c** (204 mg, 400 μmol) was dissolved in dry toluene (20 cm³) in a dry Schlenk tube and the solution was saturated with carbon monoxide by bubbling the gas through the solution over a period of 5–10 min. The solution was then heated at 72 °C with the carbon monoxide atmosphere being maintained by two carbon monoxide-filled balloons. The heating was continued for 50 h by which time TLC analysis indicated that the starting material had been consumed. The solvent was removed under reduced pressure and the resulting brown residue was dissolved in diethyl ether and passed through a short column of alumina (Brockmann I, neutral; diethyl ether) to give a bright orange solution. Removal of the solvent under reduced pressure and chromatography of the microcrystalline solid residue (SiO₂; LP-Et₂O, 19:1) yielded cyclopent-2-ene-1,4-dione **4c** (83 mg, 52%) as a viscous orange–yellow oil and the lactone complex **5c** (32 mg, 15%) as a red solid that was crystallised from CH₂Cl₂–LP to give bright red crystals.

Data for **4c**: [Found: *m/z* 403.1909. C₂₆H₂₇O₄ (MH) requires 403.1909]; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1731vs (CO₂Et), 1700vs (ring C=O) and 1626w (C=C); δ_{H} 1.14 [9 H, s, C(CH₃)₃], 1.29 (3 H, t, *J* 7, CO₂CH₂CH₃), 4.37 (2 H, q, *J* 7, CO₂CH₂CH₃), 6.33 (1 H, d, *J* 16, PhCH=CH), 6.81 (1 H, d, *J* 16, PhCH=CH) and 7.25–7.65 (10 H, m, 2 × Ph); δ_{C} 14.0 (CH₂CH₃), 26.2 [C(CH₃)₃], 39.6 [C(CH₃)₃], 60.7, 62.3 [CH₂CH₃ and CC(CH₃)₃], 122.0, 126.5, 127.6, 128.0, 128.6, 128.6, 129.6, 131.4, 133.8, 136.5 (2 × Ph and PhCH=CH), 144.5, 151.9 (PhC=C(CO₂Et)), 163.2 (CO₂Et), 199.3 and 202.9 (2 × ring C=O); *m/z* (CI, NH₃) 403 (MH⁺, 100%) and 347 (M – isobutene, 60).

Data for **5c**: m.p. 130–132 °C [Found: m/z 543.1132. $C_{29}H_{27}FeO_7$ (MH) requires 543.1106]; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2061vs (C=O), 2001vs (C=O), 1745m (lactone C=O) and 1601vw (C=C); δ_{H} 1.25 (3 H, q, J 8, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.56 [9 H, s, $\text{C}(\text{CH}_3)_3$], 3.64 (1 H, d, J 9.6, PhCH=CH), 4.09 (2 H, m, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.92 (1 H, d, J 9.6, PhCH=CH) and 7.2–7.6 (5 H, m, Ph); δ_{C} 13.8 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 31.6, 31.8 [$\text{C}(\text{CH}_3)_3$], 36.8 [$\text{C}(\text{CH}_3)_3$], 52.6, 62.6 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 65.8, 83.7, 95.2, 102.1, 126.1, 127.4, 128.3, 128.8, 129.1, 129.3, 139.1, 155.8, 163.9 and 167.2; m/z (CI, NH_2) 543 (MH⁺, 3%), 476 (38), 403 [MH – Fe(CO)₃, 100] and 376 (38).

X-Ray Crystallographic Analysis of 5c.—Crystal data. Single crystals of **5c**, suitable for X-ray crystallography were grown from CH_2Cl_2 –LP. $C_{29}H_{26}FeO_7$, $M = 542.3$, monoclinic, $a = 8.351(2)$, $b = 12.129(4)$, $c = 26.237(6)$ Å, $\beta = 91.20(2)^\circ$, $U = 2657$ Å³, space group $P2_1/c$, $Z = 4$, $D_c = 1.36$ gcm^{–3}, $\mu(\text{Cu-K}\alpha) = 49.3$ cm^{–1}, $F(000) = 1128$. Red, air stable plates, dimensions 0.15 × 0.15 × 0.26 mm. The data were collected on a Siemens P3 diffractometer, ω -scan method, ($0 \leq 2\theta \leq 116^\circ$), graphite monochromated Cu-K α radiation ($\lambda = 1.54178$ Å); 3845 reflections were measured, of which 3570 were independent ($R_{\text{int}} = 2.96\%$), and 2449 observed [$|F_o| > 4\sigma(|F_o|)$]. The data were corrected for Lorentz and polarisation factors. A numerical absorption correction (face indexed crystal) was applied (maximum and minimum transmission factors 0.588 and 0.418). The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. All the hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give $R = 0.051$, $R_w = 0.049$ ($w^{-1} = \sigma^2(F) + 0.0005F^2$). The maximum residual electron density in the final ΔF map was 0.44 eÅ^{–3}, and the mean and maximum shifts/error in the final refinement cycle were 0.009 and 0.042 respectively. Computations were carried out on an NAGA 486 using the SHELXTL PC program system.¹¹ Bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Carbonylation of the Adduct 2d.—The adduct **2d** (52 mg, 100 μmol) was heated under a carbon monoxide atmosphere in toluene (5 cm³) at 72 °C as described above for the adduct **2c**. After 23 h, TLC analysis indicated that the reaction had gone to completion. After work-up, dry flash column chromatography (SiO_2 ; LP–Et₂O, 10:1) gave cyclopent-2-ene-1,4-dione **4d** as a bright yellow microcrystalline solid (22 mg, 55%) and a dark red crystalline solid (9 mg, 17%) which was tentatively identified as the lactone complex **5d** by comparison of its IR and ¹H NMR spectra with those of the lactone complex **5c**.

Data for **4d**: m.p. 46–49 °C (Found: C, 70.6; H, 6.0. $C_{24}H_{24}O_4S$ requires C, 70.56; H, 5.92%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1708vs (C=O) and 1604w (C=C); δ_{H} 1.15 [9 H, s, $\text{C}(\text{CH}_3)_3$], 3.34 (3 H, s, SO_2CH_3), 6.30 (1 H, d, J 16, PhCH=CH), 6.82 (1 H, d,

J 16, PhCH=CH) 7.32–7.37 (5 H, m, Ph) and 7.42–7.61 (5 H, m, Ph); δ_{C} 26.2 [$\text{C}(\text{CH}_3)_3$], 40.3 [$\text{C}(\text{CH}_3)_3$], 43.9 (SO_2CH_3), 61.5 [CCBu⁺], 121.1, 125.7, 126.5, 127.9, 128.3, 128.7, 131.0, 132.1, 134.3, 136.1 (2 × Ph and PhCH=CH), 147.8, 157.2 (PhC=CSO₂Me), 197.9 and 200.8 (2 × C=O); m/z (EI) 352 (M⁺ – isobutene, 59%), 273 (M – isobutene – SO₂Me, 24) and 129 (100).

Data for **5d**: $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2186m (C=O), 2059m (C=O), 1999m (C=O), 1747mw (lactone C=O) and 1600vw (C=C); δ_{H} 1.60 [9 H, s, $\text{C}(\text{CH}_3)_3$], 2.52 (3 H, s, SO_2CH_3), 4.26 (1 H, d, J 10, PhCH=CH), 5.99 (1 H, d, J 10, PhCH=CH) and 7.3–7.5 (5 H, m, Ph).

Carbonylation of the Adduct 2e.—The adduct **2e** (27 mg, 50 μmol) was heated in toluene (3 cm³) under an atmosphere of carbon monoxide at 72 °C for 22 h according to the procedure described above for the adduct **2c**. Filtration through a short plug of alumina afforded a yellow–brown residue whose ¹H NMR spectrum contained none of the resonances expected for the desired cyclopentendione but only those of the starting material **2e**. No decomposition was observed. Starting material was not recovered.

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* For full details of the deposition scheme see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans 1*, 1994, Issue 1.