Thermal Rearrangement Reactions of Tricarbonyliron Lactone Complexes

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A variety of tricarbonyliron lactone complexes (1)—(12) undergo thermal decomposition upon warming in deoxygenated solvents to give products arising from decarbonylation, decarboxylation, and rearrangement pathways. The products of the reactions were characterised by spectroscopic or X-ray crystallographic methods, or in some cases, by independent synthesis. Mechanisms to account for the various transformations are also proposed.

In a preliminary communication [1] we have demonstrated that a number of pathways operate in the thermal decomposition of tricarbonyliron lactone complexes. Here we present the results of further studies in this area and discuss the factors which influence the course of the reactions. Of particular synthetic interest is the rearrangement of some of the iron complexes to δ-lactones under mild conditions. This result complements the previously reported conversion of tricarbonyliron lactone complexes into lactones *via* either oxidation [2] or exhaustive carbonylation procedures.[3]

RESULTS AND DISCUSSION

The tricarbonyliron lactone complexes (1)—(12) [2] were heated in the appropriate anhydrous, deoxygenated solvent (Table 1), the reactions being conveniently followed by t.l.c. Under these conditions the complex (1) was smoothly transformed into a single component, which on oxidative work-up with trimethylamine N-oxide gave the α,β-unsaturated aldehyde (13) in good yield.

Likewise thermolysis of complex (2) in benzene at 60 °C also proceeded slowly. Similar oxidative work-up, however, only gave uncharacterisable products. Alternative oxidants such as manganese dioxide and cupric chloride also failed to give a clean reaction although the aldehyde (14) could be isolated in low yield by preparative layer chromatography of the crude thermolysis solution. When the reaction was carried out in tetrahydrofuran (THF) under reflux, t.l.c. indicated the rapid formation of two new compounds which upon work-up were shown to be the enal (14) and the η⁴-diene tricarbonyliron complex (15). While the enal (14) could reasonably be derived from decarbonylation and rearrangement of the tricarbonyliron (2), the major product (15) must arise from decarboxylation. The complex (15) was readily characterised from its spectral data and by comparison
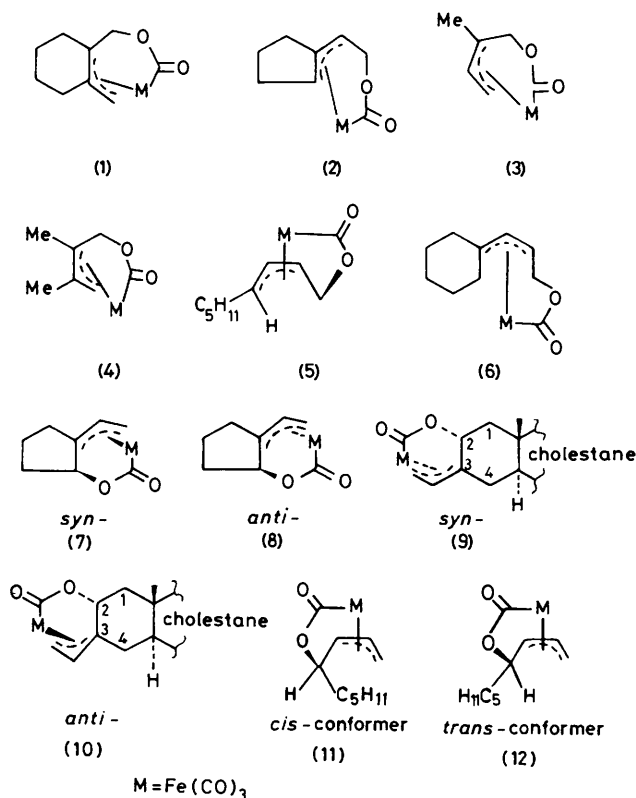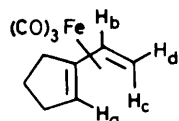

(1)   (2)   (3)

(4)   (5)   (6)

syn-   *anti*-   *syn*-
(7)   (8)   (9)

anti-   *cis*-conformer   *trans*-conformer
(10)   (11)   (12)

M = Fe(CO)₃

Thermolysis of tricarbonyliron lactone complexes

Compound	Solvent	t/h	T/°C	Products (%)
(1)	Benzene	4	60	(13) 69 [a]
(2)	Benzene	20	60	(14) 19
(2)	THF	3	Reflux	(15) 54 and (14) 23
(3)	Et$_2$O	4	80 [b]	(16) 22 [c] and [(17) + (18)] 44 [d]
(4)	Et$_2$O	4	80 [b]	(19) 6.9 [c] and (20) 59.7 [c]
(5)	THF	3	66	(21) 27
(6)	THF	3	Reflux	(22) 82
(7)	Benzene	2.5	Reflux	(15) 40
(7)	THF	2.5	Reflux	(15) 38
(8)	Benzene	12	70	(15) 7, (23) 5, (24) 9, and (25) 50
(8)	THF	2.5	Reflux	(15) 30, (24) 16, and (25) 40
(9)	THF	3	Reflux	(26) 35 and (27) 24
(10)	THF	3	Reflux	(26) 36 and (27) 37
(11)	THF	3	Reflux	(21) 39 and (29) 16
(12)	THF	3	Reflux	(21) 40 and (28) 12.5

[a] Product isolated upon oxidative work-up with trimethylamine N-oxide (see Y. Shvo and E. Hazum, J. Chem. Soc., Chem. Commun., 1974, 336). [b] Reaction carried out in a sealed bomb. [c] Determined by u.v. spectroscopy. [d] Combined yield by g.l.c. analysis. [e] By g.l.c.

with an authentic sample prepared by treatment of the uncomplexed diene with ennacarbonyldi-iron [Fe$_2$(CO)$_9$]. The ^{1}H n.m.r. spectrum exhibited characteristic resonances from H$_b$, H$_c$, and H$_d$; the inner-proton H$_c$ resonated at higher field than the corresponding outer-proton H$_d$.[4,*]

		δ	J/Hz
	H$_b$	5.35(dd)	8.7 and 6.6
	H$_c$	−0.23(dd)	8.7 and 2
	H$_d$	1.47(dd)	6.6 and 2

The tricarbonyliron lactone complexes (3) and (4), on warming in diethyl ether, afforded products derived from decarbonylation and decarboxylation pathways. The products were characterised by g.l.c. and u.v. spectroscopic techniques; the thermolysis was carried out in this case in a sealed bomb to avoid loss of volatile products. The derived tricarbonyliron diene complexes (16) and (19) were separately identified by their g.l.c. retention times,[3] and their yields determined by comparative u.v. spectroscopy.[5]

The isomeric enal complexes (17) and (18), from the lactone complex (3), were separable by p.l.c. in the ratio 1 : 2.2, their structural assignment being based upon spectral properties.

The minor isomer (17) exhibited in its ^{1}H n.m.r. spectrum a resonance corresponding to the terminal methyl

* The nomenclature anti is used consistently in the literature to denote this type of geometry. However, in the case of methylene termini, this nomenclature becomes confusing and therefore the terms inner- (anti) and outer- (syn) will be used to denote such protons.

group ca. 0.7 p.p.m., to higher field than the related methyl group resonance in the major isomer (18), indicating a closer proximity to the tricarbonyliron moiety. Irradiation of 2-methylbut-2-enal (tigaldehyde) in the presence of pentacarbonyliron gave a η^4-tricarbonyliron complex which was identical in all respects (^{1}H n.m.r. spectrum and t.l.c.) with complex (18). Thermal decomposition of the complex (5) in THF afforded the diene complex (21), as the only isolable product, by an analogous reaction pathway.

While thermal treatment of the complexes (1)—(5) gave α,β-unsaturated carbonyl compounds and/or their corresponding tricarbonyliron diene complexes, the complexes (6)—(12) on similar treatment behaved rather differently. Thus, complex (6), on heating to reflux in THF, produced the stable dienol complex (22) in 82% yield. The geometry of the hydroxy-group was assigned anti * on the basis of the magnitude of the coupling constant between the neighbouring olefinic protons (J_{cis} 7.6 Hz).

On warming the tricarbonyliron complex (7) in either benzene or THF the only product that could be isolated was the diene complex (15); however, the anti-complex (8) gave a range of products and was clearly very sensitive to change in the reaction conditions (Table 1). From a synthetic point of view we were especially pleased to see the formation of δ-lactones (24) and (25), in the thermolysis of complex (8), although the yields of these products were not high. In addition, in the reaction of complex (8) in benzene, a novel tetracarbonyliron complex (23) was formed. The structure of this complex (23) could not be unambiguously determined from its spectral and microanalytical data, and consequently we resorted to X-ray crystallographic analysis (Figure and Tables 2, 3, and 4). When the complexes (9) and (10) were heated under reflux in THF similar product ratios of compounds (26) and (27) were obtained. In these examples the corresponding tricarbonyliron diene complexes were not observed as products. The structure of the alkene (26) was assigned on the basis of its 400 MHz ^{1}H n.m.r. spectrum and the fact that it showed a molecular ion at m/z 414. Difficulty in the purification of this compound prevented its elemental microanalysis. We were also unable to obtain suitable crystals for X-ray crystallographic determination. Further spectral or chemical methods to characterise fully compound (26) were not attempted.

Thermal decomposition of complexes (11) and (12) gave diene complexes and δ-lactones, as in Table 1.

Any mechanism proposed to accommodate the above transformations must take into account the observed variation in reactivity and the diversity of products. We propose that the formation of all the non-lactonic products arises from the initial decarbonylation of the tricarbonyliron lactone complex to afford a co-ordinatively unsaturated intermediate such as complex (31), which can undergo rearrangement or collapse to complex (32) which, in turn, could react further (Scheme 1).

The formation of α,β-unsaturated aldehydes (Scheme 1;

(13)   (14)   (15)

(16)   (17)   (18)

(19)   (20)   (21)

(22)   (23)   (24)

(25)   (26)   (27)

(28)   (29)   (30)

M=Fe(CO)$_3$
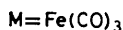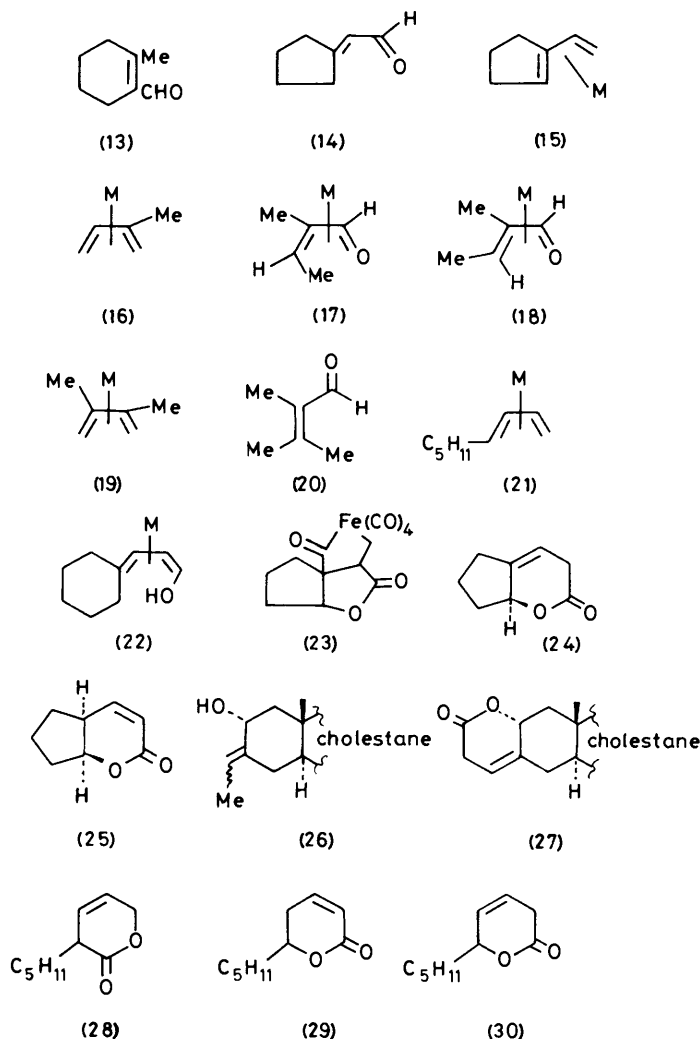
R^4 = H) would require the equivalent of a 1,4-hydrogen shift from either of the intermediates (31) and (32), which further fragment to afford the η^4-tricarbonyliron complex (33). Analogous 1,4-hydrogen shifts have been reported in the case of the decarbonylation of the lactam complex (34).[6]

Complex (6) afforded the dienol complex (22) as the only product, however, and it seems unlikely that this arose from the trapping out of the enol tautomer; thus its formation requires that the carbonyliron moiety remains co-ordinated throughout the reaction sequence. From an examination of molecular models, collapse of a co-ordinatively unsaturated species such as complex (35) would be disfavoured as a result of steric congestion between the tricarbonyliron moiety and the cyclohexane ring. Therefore, with this pathway effectively blocked, the loss of a proton to form a π-allyl anion complex (36) as a tight ion-pair, followed by reprotonation on oxygen, would afford the dienol (22). Such π-allyl anionic com-

plexes have been reported and, on protonation, do give dienol complexes.[7]

The formation of η^4-tricarbonyliron diene complexes during thermolysis is common to most systems. This reaction must result from extrusion of either carbon dioxide or an iron(II) oxide species (Scheme 2).

Analysis of the gaseous phase from a sealed-system thermolysis reaction, by i.r. spectroscopy, indicated the presence of carbon monoxide only ($\nu_{max.}$ 2 170 and 2 120 cm^{-1}); carbon dioxide ($\nu_{max.}$ 2 330 cm^{-1}) was *not* detected. Thus, it seems reasonable that the reaction proceeds with extrusion of iron oxide, possibly *via* intermediates of the type (37) and (38). The isolation of tricarbonyliron diene complexes is easily rationalised since, in most cases, η^4-enal tricarbonyliron or η^2-olefin tetracarbonyliron complexes are also formed and would readily undergo ligand exchange to afford the thermodynamically more stable diene complex. Loss of iron oxide, however, reduces the number of carbonyliron species present and,
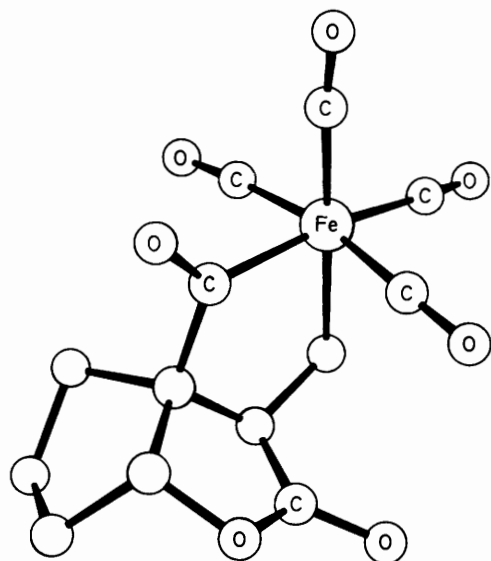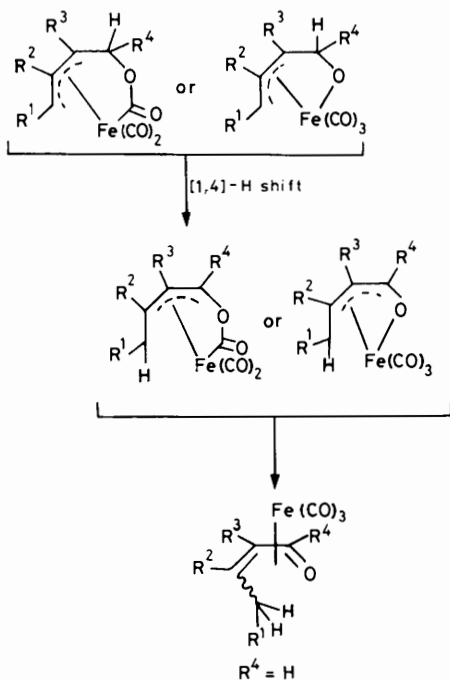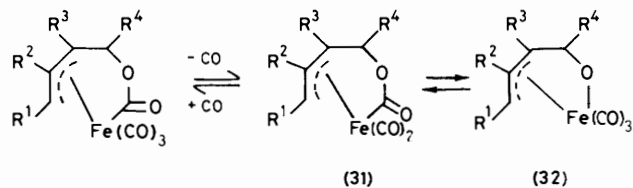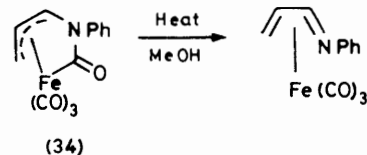
FIGURE Structure of complex (23)

therefore, for the above mechanism to operate, the yields of tricarbonyliron diene complexes must not exceed 50%. This fact is true for all cases studied, the 54% yield for the diene complex (15) being within the limits of experimental error.

Interestingly, thermolysis of the tricarbonyliron lactone complexes (11) and (12) gives rise to only one diene complex (21). This result indicates that the initial stereochemical features of the complexes are not maintained during the course of the reaction and implies equilibration of the intermediates prior to the extrusion of iron oxide.
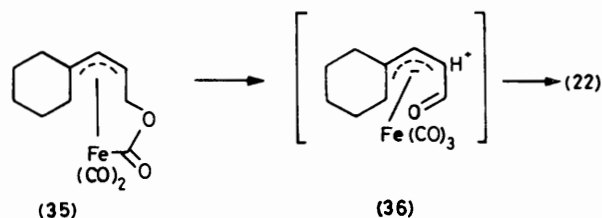
When $R^4 \neq H$, α,β-unsaturated carbonyl compounds are not observed, and it therefore follows that there is a delicate balance between several competing pathways, substitution at C-4 being sufficient to tip this balance. If the decarbonylation pathway could be suppressed, δ-lactones might be expected to be the sole products from a number of the complexes. Consequently on treating the complexes (5), (11), and (12) with carbon monoxide [3,8] (195 °C, 60 atm) the δ-lactones (28), (29), and (30) were obtained.

The lactone (29) formed from complex (11) in 65% yield was identical with the natural product massoialac-
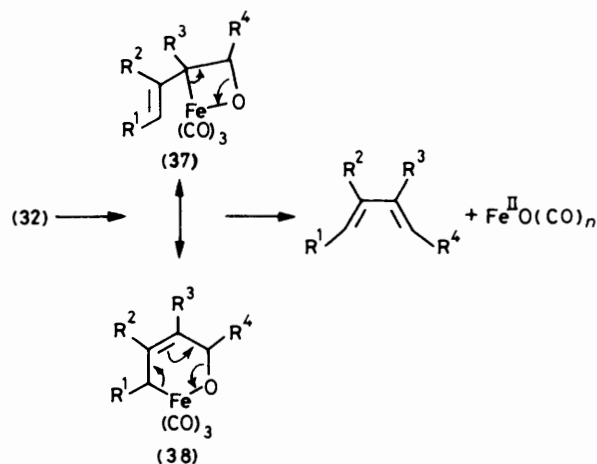

SCHEME 1 Formation of α,β-unsaturated aldehydes from tricarbonyliron lactone complexes

SCHEME 2 Formation of dienes from tricarbonyliron lactone complexes

tone, which was first isolated from the essential oil of the bark of *Cryptocarya massoia* L.[9]

The α,β-unsaturated lactone (28) could be converted into (±)-massoialactone by treatment with $Fe_2(CO)_9$ in boiling di-n-butyl ether. These results suggest that the initial product in these reactions is the β,γ-unsaturated lactone which subsequently rearranges to the thermodynamically more stable α,β-unsaturated δ-lactone.

In conclusion therefore it has been shown that a number of pathways operate in the thermal reactions of tricarbonyliron lactone complexes.

EXPERIMENTAL

M.p.s were determined on a Kofler block and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer 298 spectrometer. N.m.r. spectra were recorded with a Varian E. M. 360A, XL-100 or Brucker WH250 spectrometer. Spectra were obtained for solutions in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were recorded with a V. G. Micromass 7070 spectrometer. All reaction solvents were purified before use.

Tricarbonyliron Lactone Complexes.—These were obtained by photolysis of the corresponding vinyl oxiran in the presence of pentacarbonyliron according to previously determined procedures.[2]

General Procedures for the Thermolysis of Tricarbonyliron Lactone Complexes.—The tricarbonyliron lactone complex was combined with the appropriate anhydrous, degassed solvent (benzene or THF) and heated at the required temperature with stirring under an atmosphere of argon until t.l.c. examination showed complete disappearance of the starting material. The solvent was distilled off at atmospheric pressure and the residue subjected to preparative layer chromatography (p.l.c.) on silica gel.

Thermolysis of Tricarbonyl-α—2-η³-[formyloxymethyl(o-methylene)cyclohexylato]iron (1).—The complex (1) (100 mg, 0.34 mmol) was heated at 60 °C in benzene (10 ml). On completion of the reaction (4 h), trimethylamine N-oxide (205 mg, 2.74 mmol) was added, and the resultant mixture heated under reflux for 4 h. P.l.c. of the crude product yielded 2-methylcyclohexene-1-carbaldehyde (13) (29.2 mg, 69%), $v_{max.}$ 2 850, 1 660, 1 635, 1 360, 1 275, 1 240, 1 140, 1 060, and 740 cm⁻¹; δ 9.98 (1 H, s), 2.28—1.72 (7 H, m), and 1.7—1.23 (4 H, m).

Thermolysis of Tricarbonyl-α—2-η³-[cyclopent-1-enyl(formyloxy)methylato]iron (2).—(a) Complex (2) (160 mg, 0.58 mmol) in benzene (16 ml) at 60 °C for 20 h afforded, after p.l.c., cyclopentylideneacetaldehyde (14) (12 mg, 19%), $v_{max.}$ 2 960, 2 870, 2 840, 2 760, 1 670, 1 650, 1 610, 1 150, and 1 095 cm⁻¹; δ 9.73 (1 H, d, J 8 Hz), 5.9 (1 H, dt), 3.0—2.33 (4 H, m), and 2.0—1.5 (4 H, m).

(b) Complex (2) (200 mg, 0.72 mmol) in THF (20 ml) under reflux for 3 h gave, after p.l.c., (i) η⁴-1-vinylcyclopentene-tricarbonyliron (15) (90.2 mg, 54%), $v_{max.}$ 2 950, 2 860, 2 020, 1 980—1 930, 1 420, 1 190, and 1 160 cm⁻¹; δ 5.25 (1 H, dd), 2.07—1.57 (7 H, m), 1.47 (1 H, dd), and −0.23 (1 H, dd); and (ii) cyclopentylideneacetaldehyde (14) (17.8 mg, 23%), $v_{max.}$ 2 940, 2 860, 2 750, 1 670, 1 615, 1 175, 1 155, and 840 cm⁻¹; δ 9.72 (1 H, d, J 8 Hz), 5.9 (1 H, dt, J 8 and 2 Hz), and 2.93—1.47 (8 H, m).

Thermolysis of Tricarbonyl[formyloxymethyl(vinyl)ethylato]iron (3).—Complex (3) (200 mg, 0.79 mmol) was com-

bined with diethyl ether (20 ml) in a sealed bomb and heated at 80 °C. Upon completion of reaction (4 h) the solvent was removed by distillation at atmospheric pressure. Reaction yields were determined by g.l.c. and u.v. spectroscopic analysis of the crude reaction product; the pure materials were isolated by p.l.c., affording tricarbonyl-η⁴-isopreneiron (16) (22%), $λ_{max.}$ 220 nm (log₁₀ ε 4.38),[10] and by g.l.c.[3] to give tricarbonyl-η³-anti-2-methylbut-3-enaliron (17), δ 7.44 (1 H, s), 2.36 (1 H, dq, J 7.5 and 6.5 Hz), 1.42 (3 H, d, J 6.5 Hz), and 1.28 (3 H, d, J 7.5 Hz), and tricarbonyl-η³-syn-2-methylbut-2-enaliron (18), δ 7.28 (1 H, s), 2.21 (1 H, q, J 6.5 Hz), 2.06 (3 H, s), and 1.46 (3 H, d, J 6.5 Hz), in 44% combined yield (determined by g.l.c.).

Thermolysis of Tricarbonyl[formyloxymethyl(isopropenyl)-ethylato]iron (4).—Complex (4) (100 mg, 0.38 mmol) was dissolved in diethyl ether (10 ml) in a sealed bomb and heated at 80 °C. Upon completion of the reaction (4 h) the solvent was removed by distillation at atmospheric pressure. Reaction yields were determined by g.l.c. and u.v. spectroscopic analysis of the crude reaction product, the pure materials being isolated by p.l.c. to give tricarbonyl-η⁴-2,3-dimethylbutadieneiron (19), 6.9%, $λ_{max.}$ 226 nm (log₁₀ ε 4.33),[10] and by g.l.c. giving 2,3,3-trimethylpropenal (20) (59.7%), δ 10.13 (1 H, d, J 1.5 Hz) (determined by g.l.c. using an external standard).

Thermolysis of Tricarbonyl-η³-(1-formyloxynon-3-en-2-ylato)iron (5).—Complex (5) (100 mg) in THF at 66 °C for 3 h gave, after p.l.c., tricarbonyl-η-E-nona-1,3-dieneiron (21) (23 mg, 27%), $v_{max.}$ 2 920, 2 880, 2 020, 1 990, 1 940, 1 460, 1 370, 1 150, and 1 100 cm⁻¹; δ 5.3—5.1 (2 H, m), 1.76—1.2 (9 H, m), 1.08 (1 H, dt, J 7.5 and 6.5 Hz), 0.95 (3 H, t, J 7 Hz), and 0.26 (1 H, dd, J 8.5 and 2 Hz).

Thermolysis of Tricarbonyl-1—βη³-(3-cyclohexylidene-1-formyloxypropan-2-ylato)iron (6).—Complex (6) (100 mg, 0.33 mmol) in THF (10 ml) under reflux for 3 h afforded, after p.l.c., tricarbonyl-η⁴-(anti-3-cyclohexylideneprop-1-en-1-ol)iron (22) (74 mg, 82%), $v_{max.}$ 3 605, 2 940, 2 875, 2 040, and 1 990—1 930 cm⁻¹; δ 5.12 (1 H, d, J 7.6 Hz), 3.52 (1 H, m, D₂O exchangeable), 3.38—2.3 (6 H, m), and 2.3—1.2 (6 H, m) (Found: C, 52.05; H, 5.05. $C_{12}H_{14}FeO_4$ requires C, 51.83; H, 5.07%).

Thermolysis of Tricarbonyl-1—β-η³-(syn-2-formyloxy-1-vinylcyclopentylato)iron (7).—(a) The syn-complex (7) (250 mg) in benzene (25 ml) was refluxed for 2.5 h. The crude product, after p.l.c., gave tricarbonyl-1-vinylcyclopentene iron (15) (85 mg, 40%), $v_{max.}$ 2 950, 2 860, 2 020, 1 980, 1 930, 1 420, 1 190, and 1 160 cm⁻¹; δ 5.25 (1 H, dd, J 8.7 and 6.6 Hz), 2.07—1.57 (7 H, m), 1.47 (1 H, dd, J 6.6 and 2 Hz), and −0.23 (1 H, dd, J 8.7 and 2 Hz).

(b) The syn-complex (7) (100 mg) in THF (10 ml) gave, on heating under reflux for 2.5 h, the tricarbonyldieneiron complex (15) (32 mg, 38%), identical by t.l.c., and i.r. and ¹H n.m.r. spectrometry with the previous sample.

Thermolysis of Tricarbonyl-1—β-η³-(anti-2-formyloxy-1-vinylcyclopentylato)iron (8).—(a) The anti-complex (8) (100 mg) in benzene (100 ml) was heated at 70 °C for 12 h. Separation of the crude product by p.l.c. gave (i) the tricarbonyldieneiron complex (15) (6 mg, 7%), identical with the previous sample; (ii) the tetracarbonyliron complex (23) (6 mg, 5%), m.p. 119—122 °C, $v_{max.}$ 2 100, 2 020, 1 760, and 1 675 cm⁻¹; δ 4.77 (1 H, br s), 3.18 (1 H, dd, J 7.8 and 8.5 Hz), 2.76 (1 H, dd, J 7.8 and 11 Hz), 2.63 (1 H, dd, J 8.5 and 11 Hz), and 1.99—1.6 (6 H, m) (Found: C, 46.7; H, 2.95. $C_{13}H_{10}FeO_7$ requires C, 46.74; H, 3.02%); (iii) 2-oxabicyclo[4.3.0]non-5-en-3-one (24) (4.5 mg, 9%), identical with a

previous sample; and (iv) cis-2-oxabicyclo[4.3.0]non-4-en-3-one (25) (25 mg, 50%), $v_{max.}$ 2 950, 2 880, 1 720, 1 600, 1 310, 1 150, and 1 080 cm^{-1}; δ 6.9 (1 H, dd, J 10 and 5.5 Hz), 5.93 (1 H, d, J 10 Hz), 4.95 (1 H, m), and 2.6—1.6 (7 H, m) (Found: C, 69.35; H, 7.5. $C_8H_{10}O_2$ requires C, 69.54; H, 7.3%).

(b) Complex (8) (50 mg), on heating under reflux in THF (5 ml) for 2.5 h, gave, after p.l.c., (i) the diene complex (15) (12.8 mg, 30%); (ii) the δ-lactone (24) (4 mg, 16%), and (iii) the δ-lactone (25) (10 mg, 40%).

Thermolysis of Tricarbonyl-3—β-η³-(syn-2-formyloxy-3-vinylcholestan-3-ylato)iron (9).—Complex (9) (100 mg) in THF (10 ml), on heating under reflux for 3 h, gave (i) the alcohol (26) (25.4 mg, 35%), m.p. 62—64 °C, $v_{max.}$ 3 600, 2 400, 2 920, 2 880, 1 600, 1 460, 1 440, 1 380, and 1 120 cm^{-1}; δ 5.46 (1 H, tq, J 7 and 2 Hz), 4.16 (1 H, br d, J 11 Hz), 2.33 (1 H, dd, J 14 and 3.5 Hz), 2.14 (1 H, dd, J 11.5 and 5 Hz), 1.96 (1 H, dt, J 12 and 3.5 Hz), 1.8 (1 H, tt, J 9.5 and 3.5 Hz), 1.62 (3 H, dt, J 7 and 1.5 Hz), 1.6 (1 H, br s, exchangeable), 1.55—0.9 (40 H, m), and 0.65 (3 H, s); M^+ 414; and (ii) the δ-lactone (17) (18.4 mg, 24%) identical, by t.l.c., m.p., and ^{1}H n.m.r. spectra, with the previous sample.

Thermolysis of Tricarbonyl-3—β-η³-(anti-2-formyloxy-3-vinylcholestan-3-ylato)iron (10).—Complex (10) (100 mg), upon heating in THF (10 ml) for 3 h, gave (i) the alcohol (26) (26.2 mg, 36%) and (ii) the δ-lactone (27) (28.4 mg, 37%).

Thermolysis of Tricarbonyl-1—3-η³-(cis-4-formyloxynon-1-en-3-ylato)iron (11).—The cis-complex (11) (100 mg) in THF (10 ml) was refluxed for 3 h. The crude reaction product gave, after p.l.c., (i) tricarbonyl-E-nona-1,3-dieneiron (21) (34 mg, 39%), $v_{max.}$ 2 920, 2 880, 2 020, 1 990—1 940, 1 460, 1 370, 1 150, and 1 100 cm^{-1}; δ 5.3—5.1 (2 H, m), 1.76—1.2 (9 H, m), 1.08 (1 H, dt, J 7.5 and 6.5 Hz), 0.95 (3 H, t, J 7 Hz), and 0.26 (1 H, dd, J 8.5 and 2 Hz) (Found: M^+, 264.0442. $C_{12}H_{16}FeO_3$ requires M, 264.0449); and (ii) 3,6-dihydro-3-pentyl-2-pyrone (28) (8.7 mg, 16%), $v_{max.}$ 2 920, 2 880, 1 730, 1 460, 1 370, 1 150, 1 120, and 1 060 cm^{-1}; δ 5.85 (2 H, br s), 4.96 (1 H, m), 3.05 (2 H, d, J 5 Hz), 1.75—1.2 (8 H, m), and 0.9 (3 H, t, J 7 Hz) (Found: M^+, 168.1150. $C_{10}H_{16}O_2$ requires M, 168.1150).

Thermolysis of Tricarbonyl-1—3-η³-(trans-4-formyloxynon-1-en-3-ylato)iron (12).—Complex (12) (100 mg) was combined with THF (10 ml) and heated under reflux for 3 h. Distillation of the solvent followed by p.l.c. of the residue afforded (i) diene iron complex (21) (34.7 mg, 40%), and (ii) the δ-lactone (28) (6.8 mg, 12.5%), identical with the samples obtained earlier.

Preparation of (±)-5,6-Dihydro-6-pentyl-2-pyrone [(±)-Massoialactone] (29).—(a) The tricarbonyliron lactone complex (11) (100 mg, 0.32 mmol) was combined with dry degassed benzene (10 ml) and heated in a bomb under CO (60 atm) at 195 °C for 4 h. The pressure was then released and the crude product isolated by removal of the solvent. Column chromatography on silica gel afforded (±)-massoialactone (29) (35.6 mg, 65%), $v_{max.}$ 1 720 cm^{-1}; δ 6.83 (1 H, dt, J 10 and 4.7 Hz), 5.95 (1 H, dt, J 10 and 1.6 Hz), 4.33 (1 H, m), 2.3 (2 H, m), 1.07—1.93 (8 H, m), and 0.87 (1 H, br s) (Found: C, 71.45; H, 9.85. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.87%).

(b) The tricarbonyliron lactone complex (12) (50 mg, 0.16 mmol) was combined with dry degassed benzene (5 ml) and heated in a bomb at 195 °C for 4 h under CO (60 atm). Removal of the solvent gave a mixture of the δ-lactone (28) and massoialactone (29) (18 mg, 65%) which was combined

with dibutyl ether (3 ml) and Fe_3CO_9 (108 mg, 31 mmol) and heated under an atmosphere of argon at 140 °C for 4 h. The cooled reaction mixture was filtered, the precipitate washed with diethylether and the combined filtrate and washings evaporated under reduced pressure. P.l.c. of the residue

TABLE 2

Atom co-ordinates (×10⁴) and temperature factors Å² (×10³)

Atom	x	y	z	U
Fe	406(1)	2 243(1)	605(1)	30(1)
C(1)	−7(2)	1 114(3)	1 837(5)	41(1)
O(1)	−235(2)	394(2)	2 607(4)	65(1)
C(2)	1 355(2)	1 512(3)	170(5)	39(1)
O(2)	1 941(2)	1 054(2)	−67(4)	65(1)
C(3)	−377(2)	3 163(3)	1 272(5)	40(1)
O(3)	−854(2)	3 759(2)	1 704(4)	65(1)
C(4)	979(2)	3 527(3)	−634(4)	37(1)
C(5)	1 720(2)	3 962(2)	880(4)	31(1)
C(6)	1 628(2)	3 790(2)	3 031(4)	30(1)
C(7)	1 248(2)	4 737(2)	4 030(5)	40(1)
C(8)	2 016(2)	5 503(3)	4 487(6)	59(1)
C(9)	2 805(2)	4 800(3)	5 001(5)	50(1)
C(10)	2 561(2)	3 707(2)	4 099(4)	35(1)
O(11)	3 059(1)	3 397(2)	2 577(3)	47(1)
C(12)	2 596(2)	3 507(3)	733(5)	40(1)
O(13)	2 890(2)	3 276(2)	−718(4)	61(1)
O(14)	1 151(2)	2 309(2)	4 769(4)	49(1)
O(15)	−573(2)	1 970(3)	−3 482(4)	70(1)
C(16)	1 118(2)	2 752(3)	3 191(5)	31(1)
C(17)	−202(2)	2 033(3)	−1 906(6)	45(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3

Bond lengths (Å)

Fe–C(1)	1.822(4)	Fe–C(2)	1.819(3)
Fe–C(3)	1.802(3)	Fe–C(4)	2.092(4)
Fe–C(16)	2.026(3)	Fe–C(17)	1.833(4)
C(1)–O(1)	1.133(4)	C(2)–O(2)	1.122(4)
C(3)–O(3)	1.134(4)	C(4)–C(5)	1.525(4)
C(5)–C(6)	1.508(4)	C(5)–C(12)	1.512(4)
C(6)–C(7)	1.539(4)	C(6)–C(10)	1.533(4)
C(6)–C(16)	1.546(4)	C(7)–C(8)	1.539(5)
C(8)–C(9)	1.518(5)	C(9)–C(10)	1.529(4)
C(10)–O(11)	1.450(4)	O(11)–C(12)	1.349(4)
C(12)–O(13)	1.192(5)	O(14)–C(16)	1.201(4)
O(15)–C(17)	1.135(5)		

TABLE 4

Bond angles (°)

C(1)–Fe–C(2)	92.6(1)	C(1)–Fe–C(3)	94.2(2)
C(2)–Fe–C(3)	168.4(1)	C(1)–Fe–C(4)	175.1(1)
C(2)–Fe–C(4)	84.5(1)	C(3)–Fe–C(4)	88.0(1)
C(1)–Fe–C(16)	92.0(1)	C(2)–Fe–C(16)	87.0(1)
C(3)–Fe–C(16)	83.3(1)	C(4)–Fe–C(16)	83.8(1)
C(1)–Fe–C(17)	98.3(2)	C(2)–Fe–C(17)	95.3(2)
C(3)–Fe–C(17)	93.0(2)	C(4)–Fe–C(17)	86.0(1)
C(16)–Fe–C(17)	169.3(1)	Fe–C(1)–O(1)	177.5(3)
Fe–C(2)–O(2)	178.8(3)	Fe–C(3)–O(3)	178.3(3)
Fe–C(4)–C(5)	109.8(2)	C(4)–C(5)–C(6)	114.7(2)
C(4)–C(5)–C(12)	115.2(3)	C(6)–C(5)–C(12)	104.1(2)
C(5)–C(6)–C(7)	115.0(2)	C(5)–C(6)–C(10)	103.3(2)
C(7)–C(6)–C(10)	104.9(2)	C(5)–C(6)–C(16)	108.9(2)
C(7)–C(6)–C(16)	112.2(3)	C(10)–C(6)–C(16)	112.2(2)
C(6)–C(7)–C(8)	102.9(3)	C(7)–C(8)–C(9)	105.6(3)
C(8)–C(9)–C(10)	106.8(3)	C(6)–C(10)–C(9)	106.6(2)
C(6)–C(10)–O(11)	105.7(2)	C(9)–C(10)–O(11)	113.5(3)
C(10)–O(11)–C(12)	111.2(2)	C(5)–C(12)–O(11)	109.7(3)
C(5)–C(12)–O(13)	129.0(3)	O(11)–C(12)–O(13)	121.2(3)
Fe–C(16)–C(6)	115.1(2)	Fe–C(16)–O(14)	124.3(2)
C(6)–C(16)–O(14)	120.5(3)	Fe–C(17)–O(15)	175.7(3)

afforded ($\pm$)-massoialactone (29) (13 mg, 47%), identical, by t.l.c., and i.r. and ^{1}H n.m.r. spectra, with the previous sample.

Preparation of 3,6-Dihydro-6-pentyl-2-pyrone (30).—The tricarbonyliron lactone complex (6) (50 mg, 0.16 mmol) was combined with benzene (5 ml) and heated in a bomb under CO (60 atm) at 195 °C for 4 h. The pressure was released and the solvent distilled off to give the crude product, p.l.c. of which afforded the δ-lactone (30) (13.5 mg, 49.5%), $\nu_{max.}$ 2 920, 2 880, and 1 730 cm^{-1}; δ 5.82 (2 H, br s), 4.82 (2 H, dd, J 3.5 and 1.5 Hz), 3.0 (1 H, m), 2.1—1.1 (8 H, m), and 0.92 (3 H, br s) (Found: M^+, 168.1148. $C_{10}H_{16}O_2$ requires M, 168.1150).

Tricarbonyl-η-1-vinylcyclopenteneiron (15).—1-Vinylcyclopentene (500 mg, 5.3 mmol) was combined with Fe$_2$CO$_9$ (2.13 g, 5.9 mmol) in dry, degassed THF (20 ml) and heated, under reflux, under argon. On completion of the reaction (2 h, as indicated by t.l.c.) the cooled solution was filtered, the solvent removed by distillation at atmospheric pressure and the tricarbonyliron complex (15) isolated by p.l.c. (200 mg, 16%), δ 5.25 (1 H, dd, J 8.7 and 6.6 Hz), 2.07—1.57 (7 H, m), 1.47 (1 H, dd, J 6.6 and 2 Hz), and −0.23 (1 H, dd, J 8.7 and 2 Hz).

Tricarbonyl-η-syn-2-methylbut-2-enaliron (18).—2-Methylbut-2-enal (500 mg, 5.95 mmol) was combined with pentacarbonyliron (1.6 ml, 11.9 mmol) in dry, degassed diethyl ether (25 ml), under argon. The solution was irradiated with a Philips HPK 125 W Hg discharge lamp until the reaction was complete (as indicated by t.l.c.). Removal of the solvent by distillation at atmospheric pressure afforded the *tricarbonyliron complex* (18), δ 7.28 (1 H, s), 2.15 (1 H, q, J 6.5 Hz), 2.09 (3 H, s), and 1.44 (3 H, d, J 6.5 Hz) (Found: C, 42.85; H, 3.8. $C_8H_8FeO_4$ requires C, 42.9; H, 3.6%).

X-Ray Crystallographic Analysis of Compound (23).— *Crystal data.* $C_{13}H_{10}FeO_7$, M 334. Monoclinic $a = 15.749$

* For details of the Supplementary Publication Scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index Issue.

(1), $b = 12.574$ (1), $c = 6.794$ (1), $\beta = 99.47$ (1) Å, $U = 1\ 327$ Å^3, $Z = 4$. Space group $P2_1/a$.

Of the 1 368 independent reflections measured on a diffractometer using Cu-K_α radiation 120 were classed as unobserved. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data to give a final $R = 0.028$. Atomic co-ordinates, bond lengths, and bond angles are given in Tables 2—4. Observed and calculated structure factors are given in Supplementary Publication No. 23247 (11 p.).*

REFERENCES

^{1} G. D. Annis, S. V. Ley, C. R. Self, and R. Sivaramakrishnan, *J. Chem. Soc., Chem. Commun.*, 1980, 299.

^{2} G. D. Annis, S. V. Ley, C. R. Self, and R. Sivaramakrishnan, *J. Chem. Soc., Perkin Trans. 1*, 1981, 270.

^{3} R. Aumann, H. Ring, C. Kruger, and R. Goddard, *Chem. Ber.*, 1979, **112**, 3644.

^{4} E. A. Koerner Von Gustorf, F. W. Grevels, and I. Fischer, ' The Organic Chemistry of Iron,' Academic Press, London, 1976, vol. 1, p. 113.

^{5} W. G. Danben and M. E. Lorber, *Org. Mass Spectrom.*, 1970, **3**, 211.

^{6} Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron*, 1974, **30**, 839.

^{7} (a) C. H. De Puy, R. L. Parton, and T. Jones, *J. Am. Chem. Soc.*, 1977, **99**(12), 4070; (b) C. H. De Puy and C. R. Jablonski, *Tetrahedron Lett.*, 1969, 3989.

^{8} G. D Annis, S. V. Ley, R. Sivaramakrishnan, A. M. Atkinson, D. Rogers, and D. J. Williams, *J. Organomet. Chem.*, 1979, **182**, C11.

^{9} (a) S. Abe, *J. Chem. Soc. Jpn.*, 1937, **58**, 246; (b) L. Crombie, *J. Chem. Soc.*, 1955, 1007; (c) L. Crombie, *J. Chem. Soc.*, 1955, 2535.

^{10} H. E. Ungwade, ' Organic Electronic Spectral Data,' Wiley Interscience, London, 1960, vol. II.