Carbonyliron-induced Coupling of Olefins *via* Ferracyclopentane Complexes: The Photochemical and Thermal Reactions of Dimethyl Cyclobut-3-ene-*cis*-1,2-dicarboxylate with Carbonyliron Reagents

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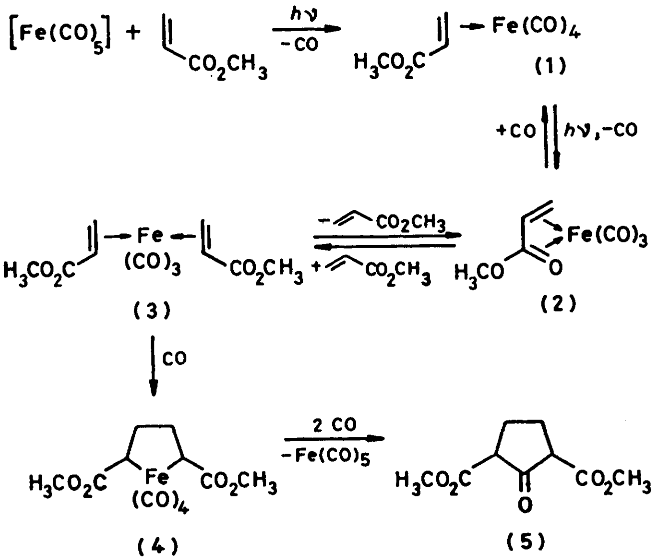
Dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate (7) reacts with $[Fe_2(CO)_9]$ (20 °C) and $[Fe(CO)_5]$ ($h\nu$, 20 °C) to form ferratricyclononane complexes (8) and (11), respectively. Subsequent insertion of carbon monoxide leads to displacement of the metal from the central five-membered ferracycle, with formation of the corresponding cyclic ketones, (9) and (12) respectively. Hydrogenolysis of the iron–carbon σ bonds is achieved by treatment of the complexes with hydrogen and Raney nickel, yielding the respective biscyclobutyl derivatives (10) and (13). Thermolysis of the complexes results in cleavage of the four-membered rings with formation of methyl acrylate and/or dimethyl fumarate. Tetracarbonyliron complexes of (7) and of cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (6) are also reported.

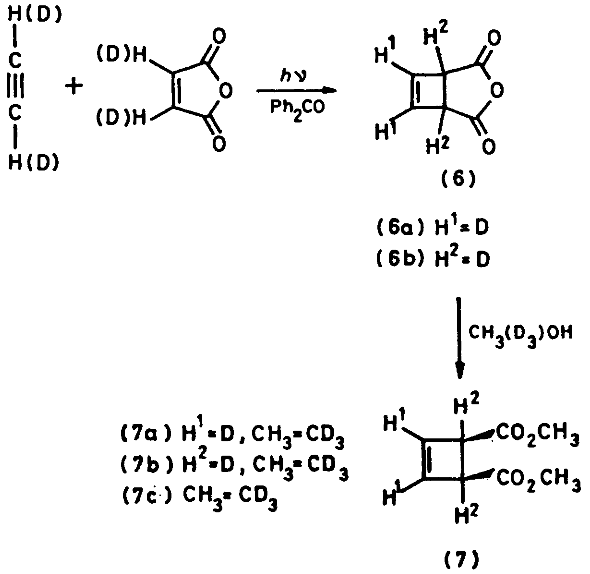
THE role of five-membered metallacycles as intermediates in transition-metal-catalysed reactions of olefins, such as cycloaddition or metathesis, is currently of interest.[1] For example, it has been proposed that the synthesis of cyclopentanone [2] and its derivatives [3-5] proceeds *via* a bis(olefin)metal complex which undergoes oxidative coupling to form a metallacycle, followed by insertion of carbon monoxide and, finally, reductive elimination of the metal.

With methyl acrylate as the olefinic substrate, pentacarbonyliron reacts photochemically to give, *via* the mono-olefin complexes (1) and (2), thermally unstable tricarbonylbis(2—3-η-methyl acrylate)iron (3) [6] which, at room temperature, is converted into tetracarbonyl-[1,4-bis(methoxycarbonyl)butane-1,4-diyl]iron (4).[6,7] Treatment of (4) with carbon monoxide yields dimethyl 2-oxocyclopentane-1,3-dicarboxylate (5).[6]

In this paper we report the thermal and photochemical reactions of a cyclic olefin, dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate (7), with nonacarbonyldi-iron and pentacarbonyliron, respectively. Compound (7) is prepared *via* the anhydride (6) from acetylene and maleic anhydride,[8] partially deuteriated (6) and (7) being readily available from the correspondingly deuteriated starting materials.



SCHEME 1



RESULTS AND DISCUSSION

At room temperature in diethyl ether and under an atmosphere of argon, the reaction of dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate (7) with $[Fe_2(CO)_9]$ yields a pale yellow crystalline tricarbonyliron complex (8). The analytical data and the mass spectrum are consistent with the formula $Fe(CO)_3(C_8H_{10}O_4)_2$. The stoicheiometry of the reaction may be described by equation (1) since evolution of carbon monoxide gas is not observed. The i.r. spectrum of (8) in n-hexane

$$\underset{(7)}{2C_8H_{10}O_4} + 2[Fe_2(CO)_9] \longrightarrow \underset{(8)}{Fe(CO)_3(C_8H_{10}O_4)_2} + 3[Fe(CO)_5] \quad (1)$$

solution exhibits three bands at 2 065.5, 1 999.5, and 1 971.5 cm^{-1} in the metal carbonyl region, ester carbonyl absorptions at 1 751.5 and 1 740 cm^{-1}, and an additional

TABLE 1

Hydrogen-1 n.m.r. data for solutions in C_6D_6

	δ													
Compound	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	CH_3			
(8) [a]	3.84	3.68	3.37	3.78	3.19	3.51	2.85	3.86			3.06	3.20	3.35	3.41
(9) [a]	3.85	2.40	3.25	3.68	2.28	3.14	3.14	2.67			3.21	3.25	3.30	3.33
(10) [b]	H^1—H^{10} : 1.3—3.5										3.88	3.39	3.40	3.45
(10a) [b]		3.07	2.76			3.28	2.80		1.56	2.46				
(11) [b,c]	3.88	3.88	3.55	3.65	3.78	1.89	3.20	1.69			3.35 (6 H);	3.42 (6 H)		
											3.70 (6 H);	3.74 (6 H) [d]		
											3.66	3.67	3.70	3.71 [e]
(12) [a]	3.29	3.38	3.72	3.10	3.38	2.03	3.01	1.13			3.24	3.35	3.38	3.42
(13) [b,c]	2.18	3.01	2.72	2.92	(=H^4)	(=H^1)	(=H^2)	1.66	(=H^8)	(=H^3)	3.43 (6 H);	3.38 (6 H)		

	J/Hz													
Compound	H^1,H^2	H^2,H^3	H^3,H^4	H^1,H^4	H^5,H^6	H^6,H^7	H^7,H^8	H^5,H^8	H^4,H^5	H^1,H^3	H^5,H^7	H^6,H^8	H^2,H^9	H^7,H^{10}
(8)	<1	8	9	9	9	11	8	9	<1					
(9)	7	9	3	7.5	~9.5	?	~10	7	<1					
(10a)		10				8.6							9	11
(11)	?	9.6	4.5	8.3	9.3	3.5	9.5	8.6	1.4	1.5	2.2	12.6		
(12)	3.6	9.5	6.5	9.5	7.3	3.5	9.0	7	1	1.5	<1	12.5		
(13a)		9.6					9.2						9.2	9.6

[a] On Bruker WH 270 instrument. [b] On Varian HA 100 instrument. [c] On Varian 56/60 instrument. [d] In $CDCl_3$. [e] In $(CD_3)_2CO$.

band at 1 640 cm^{-1} which is assigned to an end-on co-ordinated ester carbonyl group.[9]

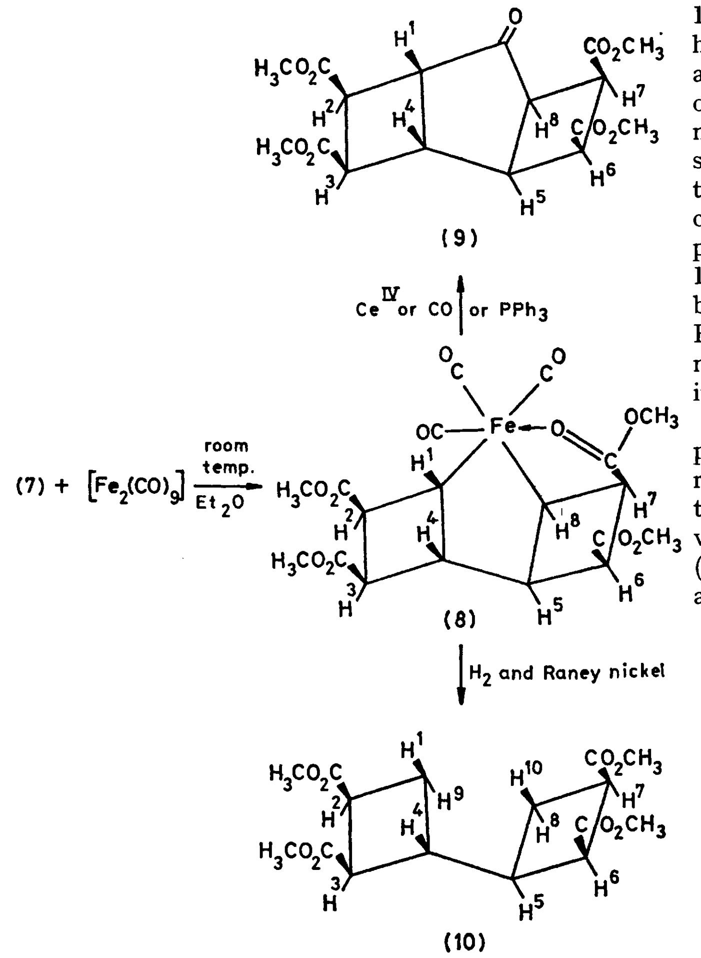
Oxidation of (8) with ammonium cerium(IV) nitrate does not afford the starting material, olefin (7), as would be expected from a bis(olefin)iron complex, but instead the carbon monoxide insertion product $(C_8H_{10}O_4)_2CO$ (9) is formed. This is consistent with the observed evolution of carbon monoxide [*ca.* 2 mol per mol of (8)]. The same product (9) is obtained from (8) and carbon monoxide, even at atmospheric pressure and room temperature. Similarly, (9) is also accessible, in moderate yield, by treating (7) with $[Fe_2(CO)_9]$ under an atmosphere of carbon monoxide without isolation of (8). Furthermore, reaction of (8) with triphenylphosphane induces the insertion of CO and results in formation of (9). Upon treatment of (8) with hydrogen and Raney nickel, the $Fe(CO)_3$ group is removed from the organic moiety which then incorporates two hydrogen atoms to give $(C_8H_{11}O_4)_2$ (10).

From these reactions it is obvious that (8) is not a tricarbonylbis(olefin)iron complex analogous to (3), but that C–C coupling has already occurred. A tricarbonylferracyclopentane derivative is formed, and one ester carbonyl group occupies a co-ordination site at the metal. The structure of (8) shown in Scheme 2 has been confirmed by an *X*-ray structural analysis.[10] In the ^1H n.m.r. spectra of (8) and (9) (Table 1) the ring-proton patterns in both cases are partially hidden by the four methyl-ester signals. However, the interpretation is greatly simplified by selective deuteriation. Spectra of the $[^2H_{16}]$ complexes (8a) and (8b) and ketones (9a) and (9b) allow the relative assignments of neighbouring pairs of protons. From decoupling experiments with the $[^2H_{12}]$ compounds (8c) and (9c) two sets of four strongly coupling hydrogens (H^1—H^4, H^5—H^8) are identified. No significant coupling between the protons of the two cyclobutane rings is present as would be expected from the chair configuration of the tricyclic systems. With both compounds, (8) and (9), one of the two sets contains a small coupling constant [<1 Hz for (8), 3 Hz for (9)] which indicates a *trans* arrangement and identifies that particular set as H^1—H^4. The detailed assignments shown in Table 1 are deduced from assignments of particular protons in each set on the basis of the following arguments. (*a*) Complex (8): comparing H^6 and H^7, the former should be more deshielded since the ester group adjacent to H^7 is co-ordinated to the metal. By *X*-ray analysis,[10] the torsional angle between H^1 and H^2 was determined to be close to 90° which must be related to the small coupling constant $J(H^1–H^2) < 1$ Hz and thus identifies these two protons. (*b*) Ketone (9): due to the well known effect of the keto-group, H^1 and H^8 should be more deshielded and shifted to lower field than H^4 and H^5, respectively. One of the two *endo* protons, H^2, must be associated with the extraordinarily high-field resonance at δ 2.40, thus confirming the assignment of H^1.

The spectrum of (10) has not been analysed in such detail. The ten ring protons exhibit a complex pattern in the aliphatic region (δ 1.3—3.5). As expected from the *exo-trans-endo* structure of complex (8), the two cyclobutyl rings of (10) are not equivalent as indicated by the four different methyl-ester signals (Table 1). The spectrum of (10a) (Table 1, tentative assignments) shows only one specifically deuteriated species to be present, and thus demonstrates the stereospecificity of the hydrogenolysis.

Pentacarbonyliron reacts photochemically with the cyclobutene derivative (7) to form a tetracarbonyliron complex, $Fe(CO)_4(C_8H_{10}O_4)_2$ (11). Frequently observed contamination of (11) with ketone (9) indicates simultaneous formation of complex (8) and its subsequent reaction with carbon monoxide. As with (8), complex

$$2C_8H_{10}O_4 + [Fe(CO)_5] \xrightarrow{h\nu} \underset{(11)}{Fe(CO)_4(C_8H_{10}O_4)_2} + CO \quad (2)$$



(8a), (9a), (10a) $CH_3 = CD_3$; $H^1, H^4, H^5, H^8 = D$

(8b), (9b) $CH_3 = CD_3$; $H^2, H^3, H^6, H^7 = D$

(8c), (9c) $CH_3 = CD_3$

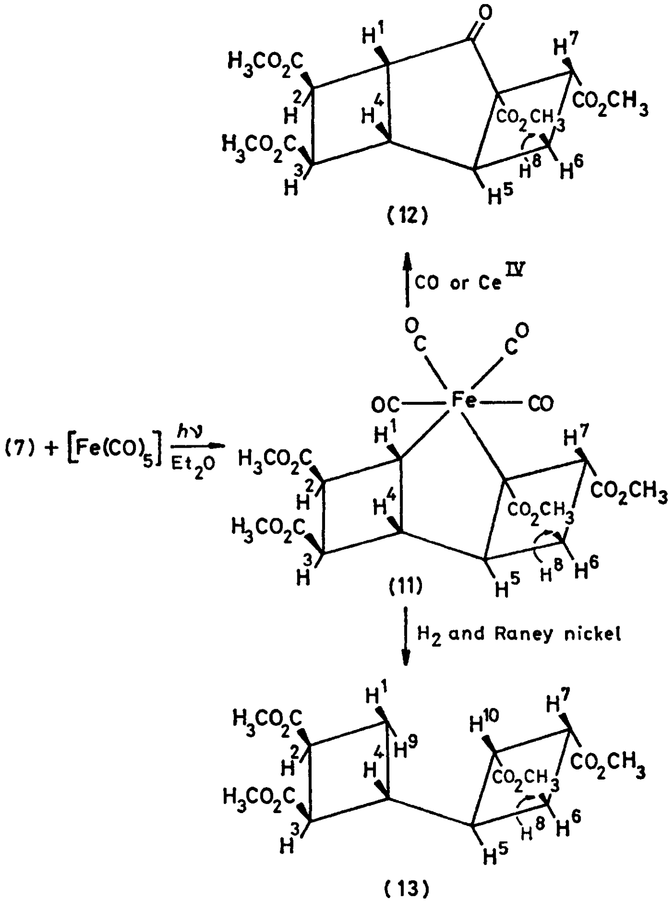
SCHEME 2

(11) is converted into $(C_8H_{10}O_4)_2CO$ (12) and $(C_8H_{11}O_4)_2$ (13) on treatment with carbon monoxide, hydrogen and Raney nickel, respectively. This indicates similar structural features for (8) and (11). The partially deuteriated compounds (11a), (11b), (11c), (12a), (12b), (12c), (13a), and (13c) have been prepared in order to simplify the interpretation of the ^1H n.m.r. spectra.

The i.r. spectrum of complex (11) shows, in addition to the characteristic $Fe(CO)_4$ pattern (2 110, 2 057, 2 038, and 2 034 cm^{-1}, in hexane), two ester carbonyl bands at 1 742 and 1 707 cm^{-1} (1 725 and 1 690 cm^{-1}, in chloroform, intensity ratio *ca.* 3 : 1). One of the four ester groups suffers a small but nevertheless significant shift to longer wavelengths [contrast complex (8)] consistent with it being attached to a carbon which is σ-bonded to iron.[6,11] Consequently, the respective cyclobutene ligand must have isomerised prior to ferracyclopentane ring closure.

Confirming this assumption, the ^1H n.m.r. spectrum of (11) (Table 1) shows two strongly coupled [$J(H^6-H^8)$ 12.6 Hz] protons at high field (δ 1.69 and 1.89) which have to be assigned to a CH_2 group. The detailed assignment of the eight ring protons follows unambiguously from the spectra of (11a) and (11b) and is in agreement with the proposed structure. In particular, the small coupling $J(H^4-H^5)$ 1.4 Hz can be clearly seen in the spectrum of (11b). This demonstrates the chair configuration and identifies H^4. The CH_2 group is also present in the ketone (12) [δ 1.13 and 2.03, $J(H^6-H^8)$ 12.5 Hz]. The differences between H^1 and H^4 and between H^2 and H^3 are analogous to those in ketone (9). Furthermore, the structural analogy of (11) and (12) is manifested by the similar coupling patterns of the individual protons.

In contrast to (11) and (12), the hydrogenolysis product (13) exhibits (Table 1) only two methyl-ester resonances and only five different ring protons, *i.e.* the two four-membered rings become equivalent by converting complex (11) into the biscyclobutyl derivative (13). This is in agreement with the structure of (11) and shows that the *cis* arrangement of the ester groups is



(11a), (12a) $CH_3 = CD_3$; $H^1, H^4, H^5, H^6 = D$

(13a) $CH_3 = CD_3$; $H^1 = H^6 = D$; $H^4 = H^5 = D$

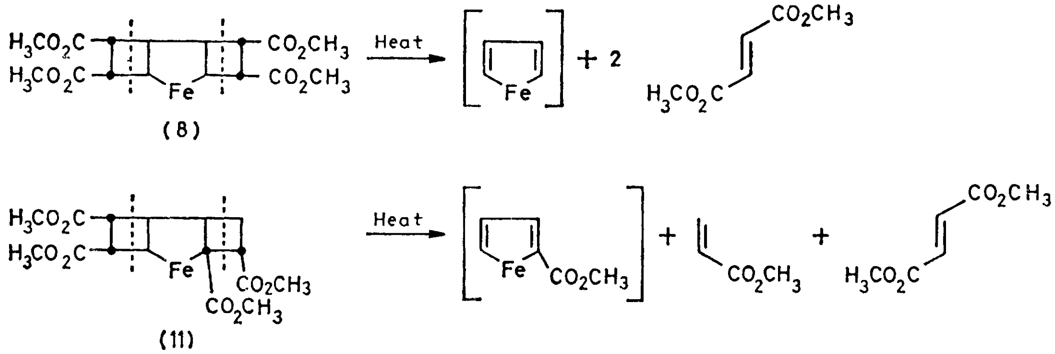
(11b), (12b) $CH_3 = CD_3$; $H^2, H^3, H^7, H^8 = D$

(11c), (12c), (13c) $CH_3 = CD_3$

SCHEME 3

retained in the course of the stereospecific hydrogenolysis. Accordingly, there are only three signals in the spectrum of (13a) which must therefore be specifically deuteriated.

Thermolysis of complexes (8) and (11) gives products resulting from the fragmentation of the four-membered rings. In particular, decomposition of (8) at 250 °C afforded dimethyl fumarate (*ca.* 6%) together with an unidentified insoluble residue and only a trace of dimethyl maleate. Assuming a *cis* configuration for the initial iron-containing fragment (see Scheme 4), this ring cleavage could be a thermal ($2\pi_a + 2\pi_s$) cycloreversion. Isomerisation of possibly formed dimethyl maleate is negligible under the reaction conditions, as checked by addition of labelled maleate in a parallel experiment (2% isomerisation). The analogous reaction of complex (11) yields a mixture of dimethyl fumarate and methyl acrylate which is further evidence for the structure shown for (11), *i.e.* for double-bond migration in one of the cyclobutene rings prior to formation of the metallacycle.



SCHEME 4

A mechanism for the formation of the ferracyclopentane complexes (8) and (11) is outlined in Scheme 5. Initially, both the *endo* (14) and the *exo* (15) co-ordinated tetracarbonyl(mono-olefin)iron complexes should be formed, thermally with $[Fe_2(CO)_9]$ and photochemically with $[Fe(CO)_5]$. Formation of the thermal *exo-trans-endo* product (8) should proceed *via* (14). Intramolecular attack of an ester group at the metal is possible in this case and could facilitate, *via* (16), the co-ordination of the second olefin. Finally, ring closure analogous to (3) ⟶ (4) (Scheme 1) gives (8) whereupon one of the *endo* ester groups takes a co-ordination site at the metal. Complex (8) is also accessible in moderate yield by short-time photolysis of $[Fe(CO)_5]$ and (7) followed by stirring the reaction mixture at room temperature in the dark, provided that the evolved carbon monoxide is removed by an argon stream. Otherwise, carbonylation of (8) occurs to give the ketone (9), as mentioned before.

Synthesis of the photoproduct (11) requires prolonged irradiation, beyond formation of the tetracarbonyliron complex (15), in order to achieve double-bond migration of the cyclobutene ligand. It is this particular photoisomerisation[12] step which results in the formation of (11) rather than of (8). Presumably, formation of an η^3-allylmetal hydride intermediate[13] from (15) is involved. The 1,3 hydrogen shift at the *exo* side of the cyclobutene diester occurs strictly stereospecifically since, as shown above, partially deuteriated (7a) and (7b) give specifically deuteriated products (11a) and (11b) with no random distribution of deuterium. The isomerised cyclobutene diester may be η^2- or η^4-co-ordinated (17) as is methyl acrylate in complexes (1) and (2), respectively. Again, the second olefinic ligand (7) is *exo* co-ordinated to the metal before ring closure occurs, followed by incorporation of CO to give (11). Some of the steps in Scheme 5 may be reversible; however, more experimental facts are required before a more detailed discussion can be made.

Attempts to isolate the proposed intermediate tricarbonylbis(olefin)iron complexes have failed. However, two complexes, (15) and a small amount of what is thought to be (16), have been separated from photolysis of $[Fe(CO)_5]$ and (7) at −40 °C. Complex (16) is characterised by the i.r. spectrum (2 048, 1 971, 1 964; 1 738, 1 645 cm^{-1}; in hexane) which indicates an end-on co-ordinated ester group [*cf.* i.r. data of (8)], and the ^{1}H n.m.r. data (see Experimental section) are in accordance with the proposed structure.

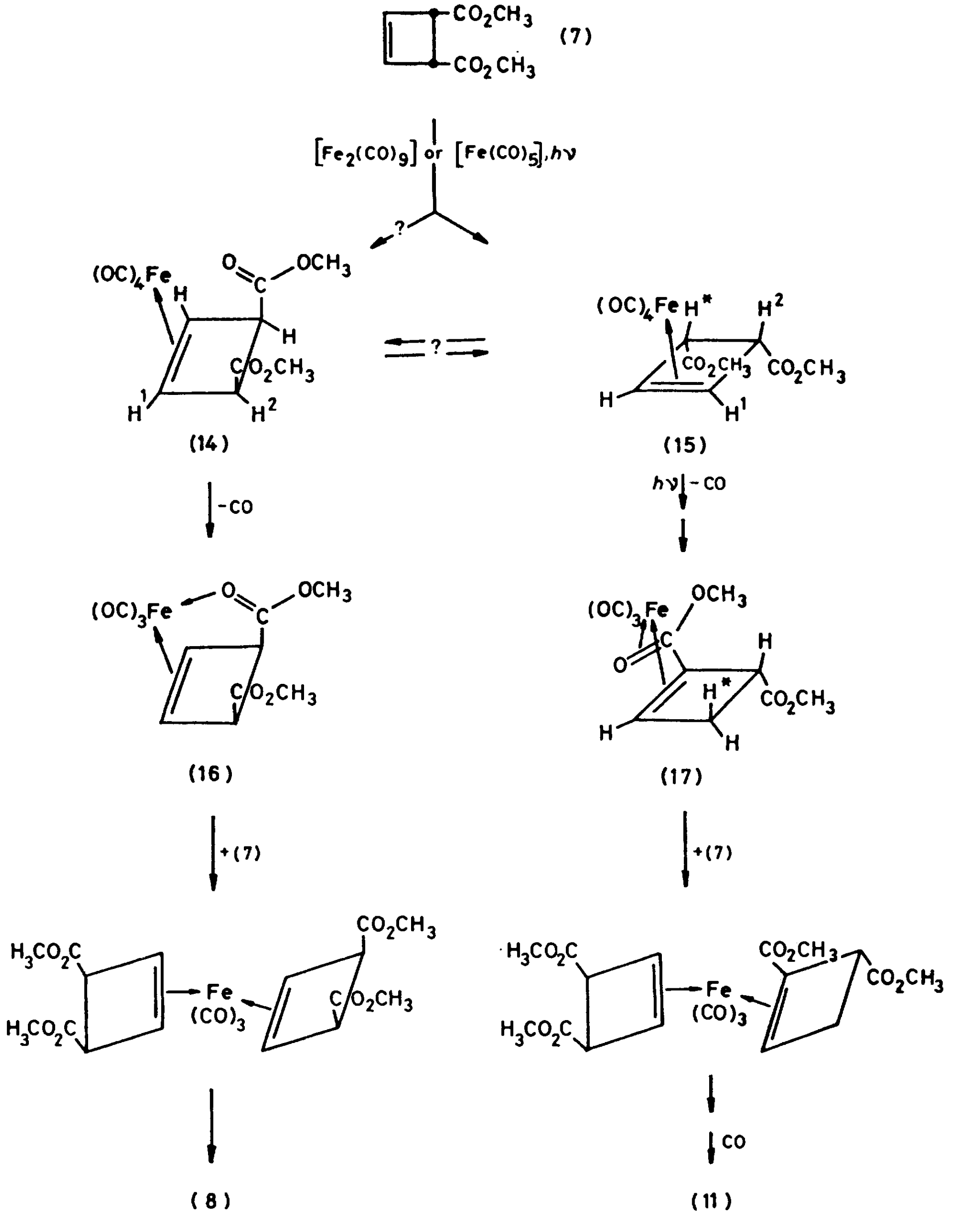
The *exo* structure (15) rather than (14) is assigned to the tetracarbonyl(dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate)iron complex by comparison of the ^{1}H

TABLE 2

Hydrogen-1 n.m.r. (δ) and i.r. data (cm^{-1}) of (15) and (18)

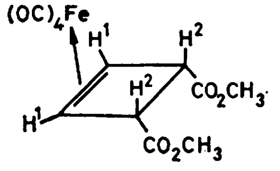
		(15)	(18)
δ	H^1	3.89 [a]	2.97 [b]
	H^2	2.95	2.43
	CH_3	3.31	
	$J(H^1-H^2)$	<1 Hz	<1 Hz
Δδ	H^1	1.92	2.50
	H^2	0.52	0.53
	CH_3	0.00	
ν(CO)		2 093.5 [c]	2 099.5 [d]
		2 024.5	2 035
		2 012	2 018.5
		1 995.5	2 005
ν(CO, ester)		1 752	
ν(CO, anhydride)			1 863.5
			1 783

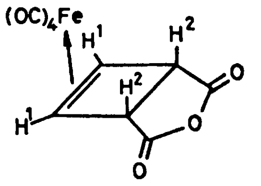
[a] In [$^2H_8$]toluene at −10 °C. [b] In C_6D_6 at room temperature. [c] In hexane. [d] In $CHCl_3$.



SCHEME 5

n.m.r. data (Table 2) with those of the anhydride complex (18), the structure of which has been determined by *X*-ray analysis.[10] In particular, the H^2 co-ordination shifts ($\Delta\delta$) are equal, whereas in (14) H^2 should be much less affected by the metal which in that case is at the opposite side of the cyclobutene ring (*cf.*, for example, the different *exo*- and *endo*-CH_2 proton shifts in metal complexes of cyclopentadiene [14] and norbornadiene [15]). Complex (15) is more conveniently accessible by reaction of $[Fe_2(CO)_9]$ with (7) in tetrahydrofuran at 0 °C. Solid (15) is stable at room temperature; however, it decomposes slowly in solution even under argon ($t_{\frac{1}{2}}$ *ca.* 80 min, *ca.* 6×10^{-3} mol dm^{-3} solution in hexane at room temperature) with formation of $[Fe(CO)_5]$ as the major carbonyliron product. This process is slightly enhanced under carbon monoxide, whereas addition of excess of olefin (7) retards the decomposition of (15). Obviously, the decomposition of (15) is initiated by breaking of the metal–olefin bond, particularly because


(15)


(18)
(18a) $H^1 = D$

in the presence of another olefin, such as methyl acrylate, ligand exchange occurs rapidly with formation of tetracarbonyl(methyl acrylate)iron (1). In view of these results, the isomerisation (15) $\leftrightarrows$ (14) (see Scheme 5) must be taken into account as an alternative to direct formation of (14). Irradiation of (15) in the presence of excess of (7) in hexane solution, as performed qualitatively in an i.r. cell, results in the formation of (11) together with a minor amount of (8).

The relatively easy formation of the tricyclic ferracyclopentane complexes from readily available starting materials offers a convenient route to specifically substituted and deuteriated biscyclobutyl derivatives and provides an alternative way to the tricyclo[5.2.0.0^{2,5}]-nonane system.[16] It is noteworthy that, for example, ketone (9) can be synthesised with >50% yield in a one-step procedure from the cyclobutene derivative (7) and [Fe(CO)$_5$] by short-time photolysis (without removal of CO) and subsequent reaction in the dark.

The anhydride complex (18) is prepared in moderate yield (<20%) by reaction of cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (6) with [Fe$_2$(CO)$_9$] in benzene. Assignment of the ^{1}H n.m.r. resonances (Table 2) is made by comparison with the spectrum of (18a). Elimination of the anhydride group of (18) could provide an alternative route to (cyclobutadiene)tricarbonyliron,[17-19] especially since the corresponding photofragmentation of matrix-isolated (6) has been reported.[20] Several attempts have been made to achieve this, including thermolysis and u.v.- and γ-irradiation of (18) but as yet without success.

EXPERIMENTAL

Spectra were recorded on the following instruments: ^{1}H n.m.r., Bruker WH 270, Varian HA 100, and A 56/60, chemical shifts (δ) being downfield from SiMe$_4$; i.r., Perkin-Elmer 621, 521, and 257; u.v., SEM Brückl HRS 4001 C; mass spectra, Varian MAT CH5. Elemental analyses and molecular-weight determinations were performed by Dornis & Kolbe, Mülheim a.d. Ruhr, and Beller, Göttingen.

Organoiron compounds were prepared and handled under argon atmospheres. Photoreactions were conducted in a Solidex glass immersion-lamp apparatus using a Philips HPK 125-W mercury lamp.

Materials.—Analytical grade solvents (Merck) were used without further purification. Pentacarbonyliron was donated by the BASF Aktiengesellschaft. Nonacarbonyldi-iron was prepared (*cf.* ref. 21) by irradiation of [Fe(CO)$_5$] in glacial acetic acid; the product was washed with ethanol, benzene, and diethyl ether and dried *in vacuo*.

Cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (6) was prepared by benzophenone-sensitised irradiation of acetylene and maleic anhydride in acetone at -70 °C.[8] The 1,2- and 3,4-dideuterio-compounds (6a) and (6b) were analogously prepared using CD≡CD (prepared from calcium carbide and deuterium oxide) and [^{2}H$_2$]maleic anhydride [22] (4.1% [^{2}H$_0$], 13.5% [^{2}H$_1$], 82.4% [^{2}H$_2$], mass spectral analysis), respectively. Dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate (7) was obtained from (6) by stirring it at room temperature in methanol which contained 2% sulphuric acid. Distillation after the usual work-up procedure was carried out at 30—40 °C (10^{-3} Torr) * in order to prevent thermal isomerisation of (7) to *cis,trans*-muconic ester.[23] The [^{2}H$_{16}$]- and [^{2}H$_{12}$]-derivatives (7a), (7b), and (7c) were analogously prepared from (6a), (6b), and (6c), respectively, using CD$_3$OD and D$_2$SO$_4$. The ^{1}H n.m.r. spectra indicated $\geqslant$99% deuteriation of the ester groups, $\geqslant$96% 1,2-deuteriation of (7a), and $\geqslant$90% of 3,4-deuteriation of (7b).

*Reactions of Dimethyl Cyclobut-*3*-ene-*cis-1,2*-dicarboxylate* (7) *with Nonacarbonyldi-iron.*—(*a*) *Formation of complex* (8) *in diethyl ether at room temperature.* Nonacarbonyldi-iron (19.67 g, 54 mmol) and (7) (9.19 g, 54 mmol) were stirred in diethyl ether (800 cm^3) at room temperature in the dark for 21 h. A dark brown flocculent precipitate (2.60 g) was filtered off, and the filtrate was concentrated to *ca.* 100 cm^3 whereupon fine yellow crystals of (8) appeared. These were filtered off, washed with ether, and dried *in vacuo* (3.73 g, 28.8%), m.p. 108—110 °C (decomp.) [Found: C, 47.55; H, 4.20; Fe, 11.7%; *M*, 461 (vaporimetry in benzene). C$_{19}$H$_{20}$FeO$_{11}$ requires C, 47.5; H, 4.20; Fe, 11.65%; *M*, 480.2]. The mass spectrum (base peak *m/e* 28, CO) showed peaks at *m/e* 424 ($P - 2$ CO), 396 ($P - 3$ CO), followed by a complicated fragmentation pattern with prominent peaks at *m/e* 368, 337, 309, 283, 248, 231, 220, 189, 164, 145, 111, 74, 59, and 45. Ultraviolet spectrum in diethyl ether: 22 000 (sh) (100), 27 450 max. (2 250), and 43 000 cm^{-1} (ε 14 000 dm^3 mol^{-1} cm^{-1}). The yield of (8) did not exceed 34% in any experiment, due to a secondary reaction of (8) with [Fe$_2$(CO)$_9$] which occurs under the reaction conditions to give the unidentified brown flocculent material mentioned above. The deuteriated complexes were synthesised analogously: (8a) (0.60 g, 31%) from [Fe$_2$(CO)$_9$] (2.89 g, 7.9 mmol), (7a) (1.41 g, 7.9 mmol), in diethyl ether (220 cm^3), 22 h; (8b) (0.31 g, 34%) from [Fe$_2$(CO)$_9$] (1.35 g, 3.7 mmol), (7b) (0.66 g, 3.7 mmol), in diethyl ether (100 cm^3), 22 h; (8c) (0.16 g, 22%) from [Fe$_2$(CO)$_9$] (1.10 g, 3.0 mmol), (7c) (0.53 g, 3.0 mmol), in diethyl ether (50 cm^3), 17 h.

(*b*) *Isolation of tetracarbonyl*(3—4-η*-dimethyl cyclobut-*3*-ene-*cis-1,2*-dicarboxylate*)*iron* (15) *in tetrahydrofuran at* 0 °C. Nonacarbonyldi-iron (7.28 g, 20 mmol) and (7) (3.40 g, 20 mmol) were stirred in tetrahydrofuran (thf) (300 cm^3) at 0 °C in the dark for 90 h. During the work-up procedure the temperature did not exceed 0 °C. The solution was evaporated *in vacuo* to remove the solvent and pentacarbonyliron. The residue (5.17 g) was extracted with hexane (400 cm^3). On cooling the solution at -80 °C pale yellow crystals of (15) (0.83 g) precipitated. The extraction was repeated twice using the mother-liquor to afford additional crops of (15) (total yield 1.19 g, 17.6%), m.p. 60—61 °C (decomp.) (Found: C, 42.45; H, 3.20; Fe, 16.55. C$_{12}$H$_{10}$FeO$_8$ requires C, 42.65; H, 3.00; Fe, 16.5%). The mass spectrum (base peak *m/e* 28, CO) showed the molecular ion (*m/e* 368) and peaks at *m/e* 307 ($P -$ OCH$_3$), 282, 254, 266 ($P - n$CO; $n = 2$—4) and other prominent peaks at *m/e* 198, 194, 168, 142, 139, 111, and 59. Ultraviolet spectrum in diethyl ether (-5 °C): 38 000 (sh) cm^{-1} (ε 5 500 dm^3 mol^{-1} cm^{-1}).

(*c*) *Formation of ketone* (9) *in diethyl ether under a carbon monoxide atmosphere.* Nonacarbonyldi-iron (7.28 g, 20 mmol) and (7) (3.40 g, 20 mmol) were stirred in diethyl ether (300 cm^3) at room temperature in the dark under a carbon monoxide atmosphere (gas burette connected to the

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* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 bar = 10^5 Pa; 1 atm = 101 325 Pa.

flask) for 24 h. After an induction period of 2 h carbon monoxide was absorbed up to a total amount of 18 mmol. A dark brown flocculent precipitate (0.10 g) was filtered off, and the filtrate was evaporated *in vacuo*. The oily residue (3.24 g) was dissolved in diethyl ether (150 cm^3) and cooled to −25 °C whereupon white crystals of (9) appeared. Additional crops were obtained from the mother liquor after concentration to 70 cm^3 (0.21 g, 5.7%), m.p. 108—110 °C [Found: C, 54.95; H, 5.60; O, 39.35%; *M*, 388 (vaporimetry in benzene). $C_{17}H_{20}O_9$ requires C, 55.45; H, 5.45; O, 39.1%; *M*, 368.4]. The mass spectrum (base peak *m/e* 113) showed the molecular ion (*m/e* 368) and prominent peaks at *m/e* 337, 277, 249, 224, 192, 165, 145, 133, 85, 59, and 28. The i.r. spectrum exhibits a strong ester carbonyl band at 1 720—1 740 cm^{-1} (chloroform solution).

Photoreactions of (7) *with* $[Fe(CO)_5]$.—(*a*) *Formation of complex* (11) *by prolonged irradiation*. Pentacarbonyliron (4.86 g, 24.8 mmol) and (7) (10.13 g, 59.6 mmol) were irradiated in diethyl ether (150 cm^3) for 6.6 h. Carbon monoxide (21.8 mmol) was evolved, and pale yellow crystals of (11) appeared after 3—4 h; they were filtered off, washed with ether, and dried *in vacuo* (3.45 g, 27.4%), m.p. 110—115 °C (decomp.) [Found: C, 47.4; H, 4.10; Fe, 11.1%; *M*, 492 (vaporimetry in benzene). $C_{20}H_{20}FeO_{12}$ requires C, 47.25; H, 3.95; Fe, 11.0%; *M*, 508.2]. The mass spectrum (base peak *m/e* 28, CO) showed peaks at *m/e* 477 ($P - OCH_3$), 452 ($P - 2$ CO), 449 ($P -$ CO $- OCH_3$), 424 ($P - 3$ CO), and 396 ($P - 4$ CO), followed by a complicated fragmentation pattern with prominent peaks at *m/e* 338, 308, 283, 248, 224, 194, 164, 138, 111, 84, 59, and 41. Ultraviolet spectrum in diethyl ether: 40 000 (sh) cm^{-1} (ε 10 250 dm^3 mol^{-1} cm^{-1}). Frequently, the precipitated crystals of (11) were contaminated with (9), the carbonyl-insertion product of complex (8), which had to be separated by column chromatography. Since (11) is virtually colourless in solution, the separation was monitored with 254 nm light using a quartz column packed with silica gel which was impregnated with a fluorescent (254 nm) indicator. The crude product was dissolved in benzene and chromatographed with diethyl ether as eluant; complex (11) was first eluted followed by ketone (9).

The deuteriated complexes were synthesised analogously: (11a), 2 h irradiation of $[Fe(CO)_5]$ (1.27 g, 6.5 mmol) and (7a) (1.15 g, 6.5 mmol) in diethyl ether (70 cm^3), giving 0.19 g crude product of (9a) and (11a), pure (11a) (0.05 g, 2.9%) being separated by column chromatography; (11b), 2 h irradiation of $[Fe(CO)_5]$ (1.20 g, 6.1 mmol) and (7b) (1.08 g, 6.1 mmol) in diethyl ether (70 cm^3) affording 0.20 g crude product of (9b) and (11b) 0.16 g of which were chromatographed to yield pure (11b) (0.07 g, 5.5%); (11c), 1.3 h irradiation of $[Fe(CO)_5]$ (1.29 g, 6.6 mmol) and (7c) (1.16 g, 6.6 mmol) in diethyl ether (70 cm^3) affording 0.24 g crude product of (9c) and (11c) 0.17 g of which was chromatographed giving pure (11c) (0.07 g, 5.8%).

(*b*) *Formation of complex* (8) *after short-time irradiation*. Pentacarbonyliron (1.87 g, 9.5 mmol) and (7) (3.25 g, 19 mmol) were irradiated in diethyl ether (160 cm^3) for 0.5 h; the evolved carbon monoxide was removed by an argon stream. The solution was stirred at room temperature in the dark for 7.5 h. A dark brown flocculent precipitate was filtered off, the filtrate evaporated *in vacuo*, and the residue dissolved in diethyl ether (50 cm^3). n-Hexane (100 cm^3) was added to precipitate complex (8) (0.47 g, 10%) which, according to the i.r. spectrum, was contaminated with complex (11). Recrystallisation from diethyl ether afforded pure (8).

(*c*) *Formation of ketone* (9). Pentacarbonyliron (4.79 g, 24.4 mmol) and (7) (4.42 g, 26.0 mmol) were irradiated in diethyl ether (160 cm^3) for 2.6 h, the lamp was turned off for 13 h, irradiation continued for 8.1 h, and again the lamp switched off for 16.5 h. During the periods of irradiation a total amount of 19.7 mmol carbon monoxide was evolved of which 43% was reabsorbed during the dark reaction periods. The solution was concentrated to *ca.* 100 cm^3, filtered, and evaporated to dryness. The residue was extracted with diethyl ether (50 cm^3) and the remaining white crystals of (9) dried *in vacuo*, yield 2.81 g (58.7%).

(*d*) *Isolation of complexes* (15) *and* (16) *after irradiation at* −40 °C. Pentacarbonyliron (2.10 g, 10.7 mmol) and (7) (1.82 g, 10.7 mmol) were irradiated in diethyl ether (225 cm^3) at −40 °C for 8 h; evolution of carbon monoxide (10.1 mmol) ceased after 2 h. Work-up was performed at $\leqslant -30$ °C. A yellow unidentified precipitate (1.54 g) was filtered off which partially decomposed at room temperature (r.t.) with formation of $[Fe(CO)_5]$. The filtrate was evaporated *in vacuo* and the oily residue (1.43 g) chromatographed (column 3 × 55 cm with cooling jacket, silica gel Merck 60, 0.04—0.06 mm). The first yellow band [eluted with diethyl ether–pentane (1 : 1)] consisted of complexes (15) and (16). After evaporation of the solvent the residue (0.15 g) was treated with hexane and cooled to −78 °C affording yellow crystals of pure (15) which were filtered off at that temperature. The filtrate contained complex (16) (i.r. bands at 2 048, 1 971, 1 964, 1 738, and 1 645 cm^{-1}) which was left (after evaporation of the solvent) as a yellow oily material, contaminated with (15) (according to the i.r. spectrum). The ^1H n.m.r. spectrum shows the olefin (7) also to be present and, therefore, the following ^1H n.m.r. data of (16) are somewhat uncertain due to superposition of particular signals with those of the impurities: δ 4.55 (1 H), 3.54 (1 H), *ca.* 3.37 (1 H, 3 H), 2.92 (1 H), 2.89 (3 H), in $[^2H_8]$toluene at −10 °C.

Reactions of Complex (8).—(*a*) *With ammonium cerium*(IV) *nitrate*. A solution of ammonium cerium(IV) nitrate (28.6 g, 52.1 mmol) in ethanol (400 cm^3) was added slowly during 1.5 h to an ice-cooled suspension of (8) (5.23 g, 10.9 mmol) in ethanol (100 cm^3). Stirring was continued for 1 h at room temperature until the carbon monoxide evolution (23.2 mmol) ceased. After addition of water (2 l) the solution was saturated with sodium chloride and extracted with diethyl ether (3 × 600 cm^3). The combined ether extracts were shaken with saturated sodium chloride solution (4 × 600 cm^3), dried over magnesium sulphate, filtered, and evaporated to dryness. The residue was dissolved in acetone (20 cm^3) and the acetone solution added to pentane (600 cm^3) whereupon fine white crystals of ketone (9) were precipitated (2.56 g, 63.8%). The deuteriated complexes were similarly converted into the deuteriated ketones. Oxidation of (8a) (0.32 g, 0.65 mmol), (8b) (0.12 g, 0.24 mmol), and (8c) (0.12 g, 0.24 mmol) with ammonium cerium(IV) nitrate (1.50 g, 2.7 mmol; 0.64 g, 1.2 mmol; and 0.60 g, 1.1 mmol, respectively) afforded (9a) (0.05 g, 20%), (9b) (0.04 g, 43%), and (9c) (0.05 g, 55%), respectively.

(*b*) *With triphenylphosphane*. Triphenylphosphane (5.0 g, 19 mmol) was added to a solution of (8) (0.80 g, 1.7 mmol) in benzene (50 cm^3). The pale yellow solution quickly turned dark brown and after 10 min, on addition of light petroleum, a brown crystalline material was precipitated. Repetitive reprecipitation from benzene–light petroleum afforded pure ketone (9) (0.12 g, 19%). Carbonyliron complexes were not isolated from the mother-liquor; however, the crude product showed several i.r. bands similar to those reported for $Fe(CO)_2(PPh_3)_3$ [24,25] complexes.

(*c*) *With carbon monoxide*. A solution of (8) (0.61 g, 1.3 mmol) in methyl acetate (20 cm^3) was stirred under an atmosphere of carbon monoxide for 2 h. Absorption of CO was measured (1.6 mmol) using a burette. The solution was evaporated *in vacuo*; the i.r. spectrum of the distillate collected in a cold trap showed the formation of $[Fe(CO)_5]$. The residue was dissolved in benzene (20 cm^3) and the filtered solution was mixed with pentane (80 cm^3) whereupon fine white crystals of ketone (9) were precipitated (0.22 g, 46%). Under more drastic conditions the yield was only slightly improved. A solution of (8) (0.41 g, 0.85 mmol) in ethyl acetate (50 cm^3) was heated in an autoclave with carbon monoxide (52 bar) at 63 °C for 17 h. After evaporation of the solution *in vacuo*, the residue was dissolved in acetone (5 cm^3), filtered, and added to pentane (60 cm^3) affording fine white crystals of ketone (9) (0.17 g, 55%).

(*d*) *With hydrogen and Raney nickel*. Complex (8) (1.00 g, 2.1 mmol) and Raney nickel [prepared from 2.0 g of Ni (50%)–Al alloy (Merck) and 25 cm^3 aqueous 25% sodium hydroxide solution, successively washed with water, ethanol, and ethyl acetate] were dissolved and suspended, respectively, in ethyl acetate (120 cm^3) and placed in an autoclave which was flushed and filled (52 bar) with hydrogen and heated at 75 °C for 8 h. The resulting dark mixture was filtered and evaporated *in vacuo*. T.l.c. of the oily residue (0.86 g) showed the presence of one major product (R_F *ca*. 0.5, diethyl ether eluant) and several minor products at lower R_F values. A sample (0.22 g) of the residue was chromatographed on silica gel (25 g, Woelm 0.05—0.2 mm) using ether as eluant and monitoring by t.l.c. The fraction from 100 to 150 cm^3 contained the main product; removal of the solvent gave the biscyclobutyl derivative (10) as a white solid (0.14 g, 77%), m.p. 72—75 °C (Found: C, 56.1; H, 6.55. $C_{16}H_{22}O_8$ requires C, 56.15; H, 6.50%). The mass spectrum shows the molecular ion (*m/e* 342), a series of fragmentations characteristic of the methyl ester groups, and, among other prominent peaks, *m/e* 198 $[P - C_2H_2(CO_2CH_3)_2]$. The i.r. spectrum (in chloroform) shows a strong ester carbonyl absorption at 1 735 cm^{-1}. The deuteriated complex (8a) was analogously converted into the biscyclobutyl derivative (10a). Hydrogenolysis of (8a) (0.50 g, 1.0 mmol) in ethyl acetate (100 cm^3) with Raney nickel (from 1.0 g Ni–Al alloy) and hydrogen (60 bar, 75 °C, 8 h) afforded, after work-up and chromatography (30 g silica gel), (10a) (0.20 g, 56%).

(*e*) *Thermolysis*. Complex (8) (60 mg, 0.13 mmol) was placed in a round-bottomed flask (50 cm^3) equipped with a cooling finger (solid CO_2). The flask was immersed in an oil-bath (250 °C) and evacuated; decomposition of the contents occurred immediately, and heating was continued for 10 min while the volatile products were condensed onto the cold finger *in vacuo* (10^{-3} Torr). The condensate was dissolved in benzene (5 cm^3) and analysed by gas chromatography which showed the ratio of dimethyl fumarate and maleate to be >98 : 2; dimethyl maleate was added as an internal standard to determine the yield of dimethyl fumarate (6.3%). In an analogous experiment, a mixture of complex (8) (50 mg, 0.10 mmol) and $[^2H_6]$dimethyl maleate (50 mg) was heated *in vacuo* and the condensate analysed by gas chromatography [Varian 1700, Carbowax 20 M 60-m glass capillary column, carrier gas H_2 (0.7 atm), 100 °C, flame ionisation detector; under these conditions $[^2H_6]$dimethyl fumarate is separated from the non-deuteriated compound, as checked by gas chromatographic–mass spectrometric (g.c.–m.s. analysis): $[^2H_6]$dimethyl fumarate (0.5 mg), $[^2H_6]$dimethyl maleate (49.5 mg), and dimethyl fumarate (1.7 mg, 5.9%).

Reactions of Complex (11).—(*a*) *With carbon monoxide*. A solution of (11) (1.06 g, 2.1 mmol) in ethyl acetate (100 cm^3) was placed in an autoclave and heated under carbon monoxide pressure (50 bar) at 63 °C for 17 h. The orange-brown solution was filtered and evaporated *in vacuo*. T.l.c. of the oily residue (0.70 g) showed that the product (R_F *ca*. 0.5, ether eluant) was contaminated with some impurities (R_F *ca*. 0.8, *ca*. 0.2). A sample (0.29 g) of the crude product was chromatographed on silica gel (25 g) using diethyl ether as eluant. The fraction from 100 to 200 cm^3 contained the main product; removal of the solvent gave the ketone (12) as a white solid (0.15 g, 47%), m.p. (after recrystallisation from benzene) 91—94 °C (Found: C, 55.4; H, 5.55. $C_{17}H_{20}O_9$ requires C, 55.45; H, 5.45%). The mass spectrum shows the molecular ion (*m/e* 368), a series of fragmentations characteristic of the methyl ester groups, and, among other prominent peaks, *m/e* 224 $[P - C_2H_2(CO_2CH_3)_2]$. The i.r. spectrum (in chloroform) shows a strong ester carbonyl absorption at 1 735 cm^{-1}.

The deuteriated complexes were analogously converted into the deuteriated ketones. Solutions of (11a) (0.26 g, 0.50 mmol), (11b) (0.12 g, 0.23 mmol), and (11c) (0.24 g, 0.46 mmol) in ethyl acetate (30—40 cm^3) were heated under carbon monoxide pressure (50—55 bar) at 63 °C for 17 h and afforded the ketones (12a) (0.09 g, 47%), (12b) (0.03 g, 34%), and (12c) (0.09 g, 51%), respectively. The starting materials (11a)—(11c) had been slightly contaminated with the ketones (9a)—(9c) which were, however, easily separated from the products (12a)—(12c) by column chromatography on silica gel (20 g) using diethyl ether as eluant.

(*b*) *With ammonium cerium*(IV) *nitrate*. A solution of ammonium cerium(IV) nitrate (2.02 g, 3.7 mmol) in ethanol (35 cm^3) was added to complex (11) (0.37 g, 0.73 mmol) in ethanol (25 cm^3). Evolution of carbon monoxide (2.2 mmol) ceased after 2 h. After addition of water (150 cm^3) the solution was saturated with sodium chloride and extracted with diethyl ether (3 × 100 cm^3). The combined ether extracts were shaken with saturated sodium chloride solution (4 × 75 cm^3), dried over magnesium sulphate, filtered, and evaporated to dryness. The oily residue (0.30 g) was chromatographed on silica gel (25 g, Woelm, 0.05—0.20 mm) using ether as eluant. The fraction from 50 to 110 cm^3 was collected and, after removal of the solvent, afforded the ketone (12) (0.04 g, 15%).

(*c*) *With hydrogen and Raney nickel*. Complex (11) (1.03 g, 2.0 mmol) and Raney nickel (from 2.0 g Ni–Al alloy) were dissolved and suspended, respectively, in ethyl acetate (120 cm^3), placed in an autoclave, and heated under hydrogen pressure (65 bar) at 75 °C for 8 h. Filtration and evaporation *in vacuo* gave the crude product (0.68 g), t.l.c. (diethyl ether as eluant) of which indicated the major product at R_F *ca*. 0.6 together with a minor component (R_F *ca*. 0.2). A sample (0.26 g) was chromatographed on silica gel (25 g, Woelm, 0.05—0.20 mm) using ether as eluant. The fraction from 50 to 250 cm^3 was collected and, after removal of the solvent, afforded the biscyclobutyl derivative (13) (0.19 g, 73%) as a white solid, m.p. 106—109 °C (Found: C, 56.1; H, 6.60. $C_{16}H_{22}O_8$ requires C, 56.15; H, 6.50%). The mass spectrum (*P*, *m/e* 342) resembles that of (10). The i.r. spectrum (in chloroform) shows a strong ester carbonyl absorption at 1 735 cm^{-1}.

Deuteriated analogues were similarly prepared. Hydrogenolysis of complexes (11a) (0.31 g, 0.59 mmol) and (11c) (0.30 g, 0.57 mmol) in ethyl acetate (70 cm^3) with Raney nickel (from 0.7 g Ni–Al alloy) and hydrogen (60 bar, 70 °C, 8 h) afforded, after work-up and column chromatography on silica gel (25 g, Woelm, 0.05—0.20 mm) using diethyl ether as eluant, the biscyclobutyl derivatives (13a) (0.07 g, 33%) and (13c) (0.13 g, 64%), respectively.

(*d*) *Thermolysis*. Complex (11) (150 mg, 0.30 mmol) was placed in a round-bottomed flask (50 cm^3) equipped with a cold finger (liquid nitrogen). The flask was evacuated (10^{-3} Torr) and immersed in an oil-bath (250 °C). Decomposition of the contents occurred immediately and the volatile products were condensed at the cold finger, dissolved in benzene (5 cm^3), and analysed by gas chromatography [Varian 1400, polypropylene glycol (Fluka), 65-m glass capillary column, carrier gas N_2 (0.6 atm), 60 to 180 °C, flame ionisation detector] which showed methyl acrylate, dimethyl fumarate, and dimethyl maleate to be formed in the mol ratio 55 : 43 : 2. In an analogous experiment, a mixture of complex (11) (150 mg, 0.30 mmol) and $[^2H_6]$dimethyl maleate (82.8 mg) was similarly thermolysed. Gas chromatographic analysis of the condensate, dissolved in benzene (2 cm^3), showed that isomerisation of dimethyl maleate occurred to some extent (16%); methyl acrylate and dimethyl fumarate were found in the mol ratio 66 : 34 [9.4 and 4.8%, respectively, based on complex (11)].

Preparation of Tetracarbonyl(3—4-η-*cyclobut*-3-*ene*-cis-1,2-*dicarboxylic anhydride*)*iron*.—Cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (6) (3.48 g, 28.1 mmol) and $[Fe_2(CO)_9]$ (11.50 g, 31.6 mmol) were stirred in benzene (200 cm^3) for 65 h. After filtration, the green solution was concentrated *in vacuo* to *ca*. 20 cm^3. Pentane (150 cm^3) was added to precipitate a crystalline material which was filtered off and washed with pentane (4 × 20 cm^3) to remove dodecacarbonyltri-iron. The crude product (2.06 g) was contaminated, according to the ^1H n.m.r. spectrum, with unchanged (6) which was sublimed (50 °C, 10^{-3} Torr, 10 h) from a sample (1.87 g) of the crude product. The residue was dissolved in benzene and reprecipitated with pentane to afford fine yellow crystals of (18) (1.03 g, 14%), m.p. 114—116 °C (decomp.) [Found: C, 41.3; H, 1.45; Fe, 19.5%; *M*, 288 (vaporimetry in benzene). $C_{10}H_4FeO_7$ requires C, 41.15; H, 1.40; Fe, 19.15%; *M*, 292.0]. The mass spectrum showed peaks at *m/e* 264, 236, 208, 180 ($P - n$CO; $n = 1$—4) and, among other prominent peaks, 124 ($C_4H_4{}^{56}FeO$, determined by high resolution). Ultraviolet spectrum in diethyl ether: 37 000 (6 600), 48 000 cm^{-1} (ε 20 100 dm^3 mol^{-1} cm^{-1}). The partially deuteriated complex was similarly prepared from the anhydride (6a) (0.62 g, 4.9 mmol) and $[Fe_2(CO)_9]$ (1.82 g, 5.0 mmol) stirred in benzene (50 cm^3) for 30 h after analogous work-up, as (18a) (0.10 g, 7%).

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