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STEREOSELECTIVE ACETYLATION OF IRON CARBONYL COMPLEXES OF 5,6,7,8-TETRAKIS(METHYLENE)BICYCLO[2.2.2]OCT-2-ENE. DIENE—HETEROTRIENE TRICARBONYLIRON COORDINATION EQUILIBRIUM IN SOLUTION AND CRYSTAL STRUCTURE OF $(C_{12}H_{11}COCH_3)Fe_2(CO)_6$

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Summary

The stereospecific monoacetylation of the pentaene 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene ($C_{12}H_{12}$; I) was achieved by treating its diiron complex ($\eta^4:\eta^4$-$C_{12}H_{12}$)$Fe_2(CO)_6$ (*endo,exo*) (II) with $CH_3COCl/AlCl_3$ in dichloromethane. Addition of the electrophile CH_3CO^+ occurred exclusively at one terminal diene carbon atom bonded to the $Fe(CO)_3$ group in the *endo* position with respect to the roof-shaped ligand. An X-ray crystal structure determination of the kinetically favoured product ($\eta^4:\eta^4$-$C_{12}H_{11}COCH_3$)$Fe_2(CO)_6$ (III) showed that the *exo*-tetrahaptotricarbonyliron group is bonded to one *s-cis*-butadiene system while the *endo*-$Fe(CO)_3$ group is coordinated to one C—C double bond of the second diene system and to the oxygen atom of the (*Z*)-acetyl substituent in a trigonal bipyramidal arrangement. III isomerises in solution to the thermodynamically more stable isomer IV in which each tetrahaptotricarbonyliron group is now bonded to a diene system. The thermodynamic and kinetic parameters of this coordination equilibrium were measured by UV spectrophotometry (ΔH —4.0 ± 0.2 kcal/mol, ΔS —4 ± 1 e.u, ΔH^* 22.0 ± 0.7 kcal/mol, ΔS^* —5 ± 2 e.u). The (Z) $\rightleftharpoons$ (E) isomerisation of the acetylated complex was observed as a subsequent step when IV was heated under argon.

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Introduction

We recently reported the synthesis and spectroscopic properties of various Fe, Ru, Mo and W carbonyl complexes of the pentaene 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene ($C_{12}H_{12}$, I), as well as the crystal structure of $(C_{12}H_{12})Fe(CO)_3$(*exo*) and a kinetic study of the cycloaddition of a dienophile to the monometallic complexes of the title ligand [1,2]. One of the bimetallic complexes, i.e. the *endo,exo*-bis(tetrahaptotricarbonyliron) isomer $(C_{12}H_{12})Fe_2(CO)_6$ (II, Scheme 1) appears to be a useful synthon, since it can be substituted stereospecifically, thus the asymmetric positions of the two $Fe(CO)_3$ groups with respect to the roof-shaped organic skeleton have been used to achieve stereospecific hydroboration and deuteration of the uncoordinated endocyclic double bond by electrophiles, and to protonate regioselectively one of the two coordinated *s-cis*-butadiene systems of the pentaene [2]. We report here on the stereospecific acetylation of II as well as an X-ray crystal structure determination of $(C_{12}H_{11}COCH_3)Fe_2(CO)_6$. We shall show that Friedel-Crafts acetylation occurs preferentially at the *endo*-(diene)$Fe(CO)_3$, whereas protonation occurs exclusively at the *exo*-(diene)$Fe(CO)_3$ of II.

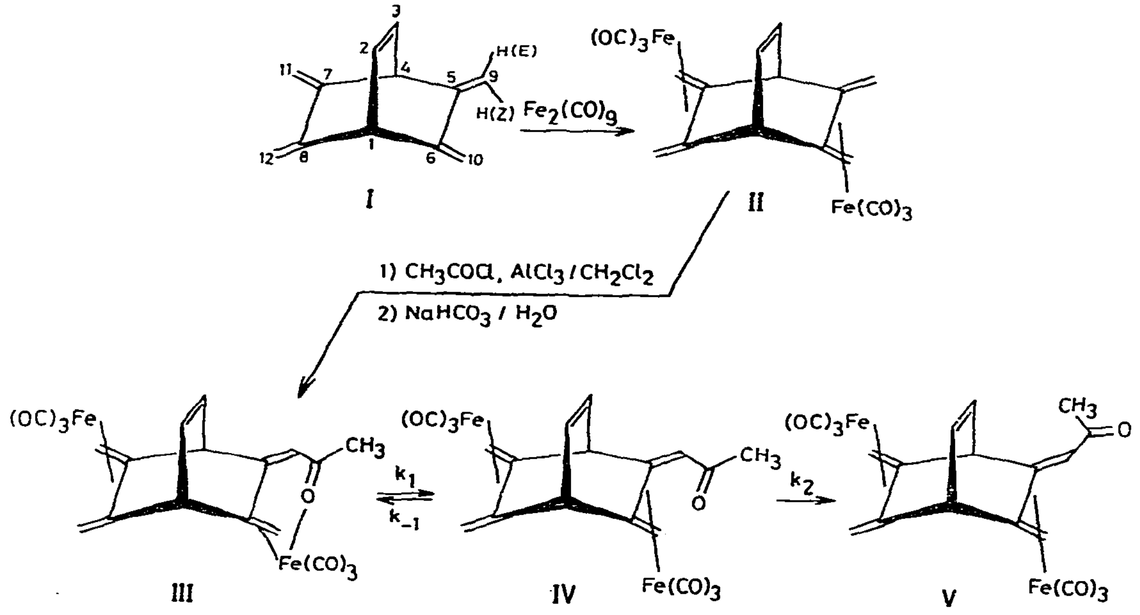
Results and discussion

Stereospecific monoacetylation of II

Electrophilic substitution of (1,3-diene)$Fe(CO)_3$ complexes was first described by Ecke who reported the acetylation of (*s-cis*-butadiene)$Fe(CO)_3$ to give 1- and 2-acetyl derivatives [3]. Subsequent work showed in fact that electrophilic attack occurs exclusively at the terminal carbon atoms of the diene [4,5] under the conditions of Friedel-Crafts acylation. Knox et al. were able to isolate the ((*Z*)-1-acetylbutadienyl)$Fe(CO)_3$ cationic intermediate prior to quenching [6]. Lillya et al. showed that the *Z*/*E* ratio of acetylated products is highly dependent on the method of quenching [7] and found optimum acetylation conditions for the synthesis of a wide variety of (dienone)$Fe(CO)_3$ complexes [7,8].

In the present case, the pentaene ligand I has a rigid carbon skeleton bearing two exocyclic *s-cis*-butadiene systems and an endocyclic C—C double bond. Complex II, a product of the reaction of I with $Fe_2(CO)_9$ [1,2], has two tetrahaptotricarbonyliron groups coordinated in *trans* positions to the two diene systems. It may act as a model for following the steric course of an acetylation reaction, since the possible sites of attack C(2), C(5), C(7), C(9) and C(11) (Scheme 1) by an electrophile are distinguishable.

Acetylation of II proceeds cleanly in dichloromethane only when $CH_3COCl/AlCl_3$ is added in stoichiometric amounts (higher ratios CH_3COCl/II lead to the partial decomposition of the starting complex). Attempts to isolate the cationic intermediate of the reaction as a tetrachloroaluminate salt were unsuccessful. Quenching with saturated aqueous $NaHCO_3/CH_3OH$ followed by extraction and chromatography revealed a single product III, which crystallised as red needles from n-hexane (57.5%). The analytical data (Experimental) for III correspond to those of a monoacetylated derivative of II. Its ^1H and ^{13}C NMR data (Table 1) were assigned by comparison of $\Delta\delta$'s (= δ(ligand) — δ(complex))



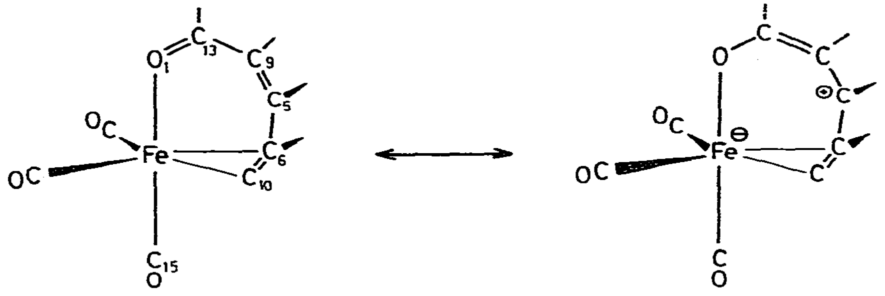
SCHEME 1

TABLE 1

^1H and ^{13}C NMR SPECTRAL DATA OF ACETYLATION PRODUCTS [a]

	III [b]	IV	V
H(1, 4) [c]	4.20, 3.33 dd [d]	4.24 m	4.27, 5.32 dd
H(2, 3)	6.98, 6.56 dd [d]	6.98 m	6.96 m
H(9)	6.12 s	3.60 s	1.10 s
H(10*E*)	3.67 d [e]	2.55 d [e]	2.29 d [e]
H(10*Z*)	0.92 d	1.66 d	0.87 d
H(11, 12*E*)	2.17, 2.02 d [f]	2.18 d [f]	2.43, 2.14 d [f]
H(11, 12*Z*)	0.67, 0.64 d	0.56 d	0.66, 0.54 d
H(14)	1.93 s (3H)	2.05 s (3H)	2.17 s (3H)
C(1, 4)	53.1, 52.1 d [g]	49.7, 49.0 d [g]	51.7, 48.4 d [g]
C(2, 3)	140.3, 131.7 d [h]	139.3, 138.4 d	140.3, 139.0 d
C(5)	178.2 s	119.5 s	111.4 s
C(6)	73.6 s	114.2 s	107.5 s
C(7, 8)	111.8, 106.4 s	110.9 s, 110.0 s	113.2, 113.0 s
C(9)	113.2 d [i]	56.3 d	44.3 d
C(10)	49.8 t [j]	43.2 t [j]	38.1 t [j]
C(11, 12)	40.1, 39.9 t [j]	40.3, 39.5 t [j]	40.9, 40.3 t [j]
C(13)	194.5 s	197.9 s	203.7 s
C(14)	28.4 q [k]	28.7 q [k]	30.2 q [k]
CO	214.2, 214.0 s, 209.8 s	209.8, 206.4 s	210.4 bs

[a] In $CDCl_3$; at −51°C for III, room temperature for IV and V; ^{13}C NMR spectrum width 3750 Hz, 4096 points. [b] Numbering scheme on Figure 1. [c] Chemical shift in ppm relative to TMS; s, singlet, d: doublet, t: triplet, q: quartet, m: multiplet. [d] $J(H(1),H(2))$ 6 Hz, $J(H(1),H(3))$ ca. 1.4 Hz, $J(H(2),H(4)) < 1$ Hz, $J(H(3),H(4))$ 6 Hz, $J(H(2),H(3))$ 6.5 Hz. [e] $J(E,Z)$ 2.4 Hz for III, 3.2 Hz for IV and V. [f] $J(E,Z)$ 3 Hz. [g] $^1J(C,H)$ 150 ± 1 Hz. [h] $^1J(C,H)$ 176 Hz for III and V, 178 Hz for IV. [i] $^1J(C,H)$ 160 ± 2 Hz for III and V, 153 Hz for IV. [j] $^1J(C,H)$ 160 ± 2 Hz. [k] $^1J(C,H)$ 128 ± 2 Hz.



SCHEME 2

with those of II [1] and by selective decoupling experiments. The endocyclic double bond C(2)—C(3) (numbering scheme on Figure 1) is uncoordinated since both ^1H and ^{13}C chemical shifts are similar to those of II. One butadiene system (H(11, 12) and C(7, 8, 11, 12)) experiences the usual shielding effect of a tetrahaptotricarbonyliron group. Of the two remaining exocyclic C—C double bonds, only C(6)—C(10) is coordinated to iron as shown by the large differences between the δ's of C(6) and C(5), C(10) and C(9), and H(10E) and H(9). Irradiations at the frequency of the H(9) signal have no detectable NOE (nuclear overhauser enhancement) on the H(10*Z*) doublet. This is expected only if H(9) is in an *E* position. The acetyl substituent is therefore in a *Z* position as geometrically required for coordination of the keto group C(13)—O(1) to the metal. The acetylated *cis*-butadiene system acts as a 4-electron donor heterotriene (left part of Scheme 2; the coordination polyhedron of Fe(1) is based on the crystal structure of III, vide infra). The high deshielding of C(5) and the unusually high shielding of C(6) indicate a substantial shift of electron density from C(5) to C(6) through the $Fe(CO)_3$ group which acts as a Lewis acid towards the vinyl ketone system (right limit structure of Scheme 2).

The NMR data of III are inconclusive as to which of the two $Fe(CO)_3$ groups is bonded to the keto group. Likewise, the low stretching frequency of the keto group (1590 cm^{-1}, compared to 1680 cm^{-1} for IV) is in accordance with a decrease in bond order through coordination but is not indicative of its mode of coordination (through a lone pair of the oxygen atom or through its π system) as a already noted by Lewis et al. for (heterodiene)$Fe(CO)_3$ complexes [9]. A crystal structure determination of III was undertaken to clarify these two points and to serve as a reference for the assignments of all the NMR spectra.

Crystal structure of $(C_{12}H_{11}COCH_3)Fe_2(CO)_6$

X-ray intensities were measured on a Syntex $P2_1$ automatic four circle diffractometer. The crystal data and the methods used are summarised in Table 2. The crystal was protected from the air by a sealed glass capillary. Its shape was accurately measured as before [10] and used to correct the intensities for absorption by the Gaussian integration method. The computer programs used for the data reduction and structure analysis were taken from the X-RAY 72 program system [11]. Scattering factors for the neutral non-hydrogen atoms were taken from Cromer and Mann [12], and for hydrogen atoms from Stewart

TABLE 2

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

Formula	$C_{20}H_{14}O_7Fe_2$	Radiation	Mo-K_α, Nb filtered (λ = 0.71069 Å)
Mol. weight	478.1	μ (cm^{-1})	15.5
Dimensions (mm)	0.07 × 0.20 × 0.22	Min and max transmission	0.74, 0.91
System	Monoclinic	Scan method	2θ—θ
a (Å)	11.155(2)	Background from	Scan profile interpretation [15]
b (Å)	9.056(1)	$(\sin\theta/\lambda)_{max}$	0.595
c (Å)	19.800(2)	Data collected	$-h, +k, \pm l$
β (°)	100.22 (1)	No. of unique reflections	3473
V (Å^3)	1968.5	No. of reflections < $3\sigma(I)$	1427
Z	4	Structure solution	Patterson and Fourier
d_{calcd} (g/cm^3)	1.61	Refinement	Block diagonal least-squares
d_{obsd} (g/cm^3)	1.60(1)	Function minimised	$\Sigma w(\|F_0\| - \|F_c\|)^2$.
F_{000}	988	w	$1/\sigma^2$
Space group	$P2_1/n$	R	0.035
Systematic absences	$h0l : h + l = 2n + 1$	R_w	0.025
	$0k0 : k = 2n + 1$	Goodness of fit	1.48

TABLE 3

ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.7121(3)	0.2062(4)	0.3323(1)	0.046(3)	0.030(2)	0.030(2)	−0.002(2)	0.005(2)	0.004(2)
C(2)	0.7538(4)	0.0760(4)	0.2989(2)	0.042(3)	0.053(2)	0.029(2)	0.002(2)	0.009(2)	−0.004(2)
C(3)	0.7396(4)	−0.0527(4)	0.3231(2)	0.046(3)	0.037(2)	0.040(2)	0.007(2)	−0.001(2)	−0.014(2)
C(4)	0.6645(3)	−0.0452(4)	0.3793(2)	0.044(3)	0.028(2)	0.034(2)	−0.003(2)	0.003(2)	0.000(2)
C(5)	0.7398(3)	0.0489(3)	0.4357(1)	0.036(2)	0.027(2)	0.035(2)	0.006(2)	0.006(2)	0.000(2)
C(6)	0.7684(3)	0.1924(3)	0.4103(1)	0.036(3)	0.031(2)	0.026(2)	0.000(2)	0.003(2)	−0.003(1)
C(7)	0.5498(4)	0.0458(4)	0.3556(1)	0.041(3)	0.038(2)	0.029(2)	−0.003(2)	0.006(2)	−0.007(2)
C(8)	0.5762(3)	0.1833(3)	0.3292(1)	0.042(3)	0.032(2)	0.023(2)	0.000(2)	0.001(2)	−0.003(1)
C(9)	0.7773(4)	−0.0052(4)	0.4998(2)	0.047(3)	0.029(2)	0.039(2)	0.001(2)	−0.001(2)	0.006(2)
C(10)	0.8714(4)	0.2790(4)	0.4374(2)	0.045(3)	0.044(2)	0.035(2)	−0.004(2)	0.001(2)	0.001(2)
C(11)	0.4265(4)	0.0093(5)	0.3560(2)	0.053(3)	0.049(3)	0.049(2)	−0.004(3)	0.013(2)	−0.004(2)
C(12)	0.4774(4)	0.2791(4)	0.3037(2)	0.057(3)	0.042(2)	0.039(2)	0.006(3)	−0.004(2)	0.000(2)
C(13)	0.8207(3)	0.0822(4)	0.5586(2)	0.040(3)	0.036(2)	0.033(2)	0.000(2)	0.002(2)	0.006(2)
C(14)	0.8873(6)	0.0094(6)	0.6229(2)	0.062(4)	0.052(3)	0.041(2)	−0.002(3)	−0.017(3)	0.010(2)
C(15)	0.6853(4)	0.4767(4)	0.4171(2)	0.058(3)	0.033(2)	0.044(2)	0.001(2)	0.008(2)	−0.006(2)
C(16)	0.7896(4)	0.5020(4)	0.5373(2)	0.071(4)	0.041(2)	0.039(2)	0.004(2)	−0.005(2)	0.001(2)
C(17)	0.5790(4)	0.3181(4)	0.4963(2)	0.062(3)	0.043(3)	0.043(2)	0.014(3)	0.010(3)	0.003(2)
C(18)	0.5187(4)	0.1225(4)	0.1854(2)	0.042(3)	0.046(2)	0.051(2)	−0.003(2)	−0.006(2)	−0.009(2)
C(19)	0.4713(4)	−0.1195(4)	0.2362(2)	0.051(3)	0.057(3)	0.037(2)	−0.002(2)	0.001(2)	−0.006(2)

C(20)	0.2971(4)	0.0967(4)	0.2213(2)	0.053(3)	0.072(3)	0.050(2)	0.002(3)	0.007(3)	−0.007(2)
Fe(1)	0.73185(5)	0.35038(5)	0.48224(2)	0.0436(4)	0.0273(2)	0.0301(2)	0.0013(3)	0.0018(2)	−0.0004(2)
Fe(2)	0.45401(5)	0.06856(5)	0.25670(2)	0.0887(4)	0.0427(3)	0.0333(3)	0.0009(3)	−0.0007(3)	−0.0054(3)
O(1)	0.7995(2)	0.2176(2)	0.56026(9)	0.051(2)	0.035(1)	0.031(1)	0.022(1)	−0.003(1)	0.002(1)
O(2)	0.6552(3)	0.5637(3)	0.3743(1)	0.101(3)	0.041(2)	0.049(1)	0.010(2)	0.006(2)	0.010(1)
O(3)	0.8237(3)	0.6027(3)	0.5701(1)	0.121(3)	0.049(2)	0.073(2)	−0.008(2)	−0.020(2)	−0.017(1)
O(4)	0.4801(3)	0.2972(3)	0.5026(2)	0.053(3)	0.089(2)	0.103(2)	0.009(2)	0.033(2)	0.009(2)
O(5)	0.5620(3)	0.1541(3)	0.1382(1)	0.857(2)	0.078(2)	0.054(2)	−0.008(2)	0.015(2)	0.002(2)
O(6)	0.4864(3)	−0.2414(3)	0.2240(1)	0.038(3)	0.051(2)	0.081(2)	−0.002(2)	0.013(2)	−0.021(2)
O(7)	0.1961(3)	0.1139(4)	0.1982(1)	0.046(2)	0.130(3)	0.091(2)	0.013(2)	0.000(2)	−0.002(2)
H(1)	0.733(3)	0.302(3)	0.316(1)	0.031(9)					
H(2)	0.311(3)	0.093(3)	0.264(1)	0.034(9)					
H(3)	0.760(3)	−0.149(3)	0.308(1)	0.029(8)					
H(4)	0.644(3)	−0.141(3)	0.396(1)	0.026(8)					
H(9)	0.764(3)	−0.104(3)	0.508(1)	0.019(8)					
H(10*E*)	0.902(3)	0.346(3)	0.404(1)	0.05(1)					
H(10*Z*)	0.924(3)	0.245(3)	0.471(1)	0.04(1)					
H(11*E*)	0.414(3)	−0.085(3)	0.358(1)	0.04(1)					
H(11*Z*)	0.378(3)	0.089(3)	0.370(1)	0.05(1)					
H(12*E*)	0.495(3)	0.360(3)	0.279(1)	0.03(1)					
H(12*Z*)	0.400(4)	0.287(4)	0.329(2)	0.09(2)					
H(141)	0.873(4)	0.061(4)	0.065(2)	0.08(1)					
H(142)	0.866(4)	−0.099(4)	0.624(2)	0.09(1)					
H(143)	0.966(4)	0.030(4)	0.626(2)	0.07(2)					

The e.s.d. of the last significant digit is given in parentheses. The temperature factor has the form e^{-T} where $T = 2\pi^2 \Sigma h_i h_j U_{ij} a^*_i a^*_j$ for anisotropic atoms and $T = 8\pi^2 U \sin^2\theta/\lambda^2$ for isotropic atoms.

TABLE 4

BOND LENGTHS (Å) IN III

Fe(1)—O(1)	1.997(2)	O(4)—C(17)	1.147(6)	C(8)—C(12)	1.420(5)
Fe(1)—C(6)	2.110(3)	O(5)—C(18)	1.162(5)	C(9)—C(13)	1.420(4)
Fe(1)—C(10)	2.030(5)	O(6)—C(19)	1.149(5)	C(13)—C(14)	1.507(5)
Fe(1)—C(15)	1.732(3)	O(7)—C(20)	1.149(5)	C(1)—H(1)	0.97(2)
Fe(1)—C(16)	1.800(3)	C(1)—C(2)	1.520(5)	C(2)—H(2)	0.95(3)
Fe(1)—C(17)	1.801(5)	C(2)—C(3)	1.307(5)	C(3)—H(3)	0.96(3)
Fe(2)—C(7)	2.068(3)	C(3)—C(4)	1.509(5)	C(4)—H(4)	0.97(2)
Fe(2)—C(8)	2.076(3)	C(4)—C(5)	1.538(4)	C(9)—H(9)	0.93(2)
Fe(2)—C(11)	2.113(4)	C(5)—C(6)	1.451(4)	C(10)—H(10*E*)	1.01(3)
Fe(2)—C(12)	2.117(4)	C(1)—C(6)	1.557(4)	C(10)—H(10*Z*)	0.86(3)
Fe(2)—C(18)	1.765(4)	C(1)—C(8)	1.518(5)	C(11)—H(11*E*)	0.90(3)
Fe(2)—C(19)	1.769(4)	C(4)—C(7)	1.530(5)	C(11)—H(11*Z*)	0.97(3)
Fe(2)—C(20)	1.784(5)	C(5)—C(9)	1.354(4)	C(12)—H(12*E*)	0.92(3)
O(1)—C(13)	1.251(4)	C(6)—C(10)	1.416(5)	C(12)—H(12*Z*)	1.07(4)
O(2)—C(15)	1.163(4)	C(7)—C(8)	1.406(4)	C(14)—H(141)	1.00(3)
O(3)—C(16)	1.146(4)	C(7)—C(11)	1.415(6)	C(14)—H(142)	1.01(3)
				C(14)—H(143)	0.89(4)
Additional distances					
Fe(1)...C(5)	2.887(3)	Fe(2)...C(3)	3.405(3)	Fe(1)...H(10*Z*)	2.40(3)
Fe(1)...C(9)	3.269(4)	C(19)...C(3)	3.234(5)	Fe(2)...H(11*E*)	2.70(3)
Fe(1)...C(13)	2.939(4)	Fe(1)...H(10*E*)	2.66(4)	Fe(2)...H(11*Z*)	2.55(3)

The e.s.d. of the last significant digit is given in parentheses.

et al. [13]. Anomalous dispersion coefficients of Fe were taken from Cromer [14]. All hydrogen atoms were found on a difference Fourier synthesis after preliminary anisotropic refinement to $R = 0.053$. Final refinement to $R =$

TABLE 5

BOND ANGLES (°) IN III

C(15)—Fe(1)—C(16)	88.6(2)	C(2)—C(1)—C(6)	104.7(3)	H(1)—C(1)—C(2)	114(2)
C(15)—Fe(1)—C(17)	93.2(2)	C(2)—C(1)—C(8)	109.2(3)	H(1)—C(1)—C(6)	109(2)
C(16)—Fe(1)—C(17)	106.1(2)	C(6)—C(1)—C(8)	105.1(3)	H(1)—C(1)—C(8)	114(2)
C(15)—Fe(1)—O(1)	174.4(3)	C(1)—C(2)—C(3)	114.3(3)	H(2)—C(2)—C(1)	119(2)
C(16)—Fe(1)—O(1)	86.9(3)	C(2)—C(3)—C(4)	114.4(3)	H(2)—C(2)—C(3)	126(2)
C(17)—Fe(1)—O(1)	91.1(3)	C(3)—C(4)—C(5)	104.8(3)	H(3)—C(3)—C(2)	128(2)
C(6)—Fe((1)—C(17)	107.3(2)	C(3)—C(4)—C(7)	108.8(3)	H(3)—C(3)—C(4)	117(2)
C(10)—Fe(1)—C(16)	106.7(2)	C(5)—C(4)—C(7)	103.7(3)	H(4)—C(4)—C(3)	115(2)
C(6)—Fe(1)—O(1)	91.3(3)	C(4)—C(5)—C(6)	112.0(2)	H(4)—C(4)—C(5)	112(1)
C(10)—Fe(1)—O(1)	86.1(3)	C(4)—C(5)—C(9)	121.0(3)	H(4)—C(4)—C(7)	111(2)
Fe(1)—C(15)—O(2)	178.6(3)	C(6)—C(5)—C(9)	126.8(3)	H(9)—C(9)—C(5)	119(1)
Fe(1)—C(16)—O(3)	176.9(3)	C(1)—C(6)—C(5)	109.9(2)	H(9)—C(9)—C(13)	116(1)
Fe(1)—C(17)—O(4)	177.3(3)	C(1)—C(6)—C(10)	119.3(3)	H(10*E*)—C(10)—H(10*Z*)	118(3)
C(7)—Fe(2)—C(8)	39.7(2)	C(5)—C(6)—C(10)	125.3(3)	H(10*E*)—C(10)—C(6)	115(2)
C(7)—Fe(2)—C(11)	39.6(2)	C(4)—C(7)—C(8)	112.3(3)	H(10*Z*)—C(10)—C(6)	119(2)
C(8)—Fe(2)—C(12)	39.6(2)	C(4)—C(7)—C(11)	129.1(3)	H(11*E*)—C(11)—H(11*Z*)	120(3)
C(11)—Fe(2)—C(12)	81.2(2)	C(8)—C(7)—C(11)	118.6(3)	H(11*E*)—C(11)—C(7)	115(2)
C(18)—Fe(2)—C(19)	90.4(2)	C(1)—C(8)—C(7)	112.0(3)	H(11*Z*)—C(11)—C(7)	115(2)
C(18)—Fe(2)—C(20)	99.1(2)	C(1)—C(8)—C(12)	129.9(3)	H(12*E*)—C(12)—H(12*Z*)	117(3)
C(19)—Fe(2)—C(20)	100.7(2)	C(7)—C(8)—C(12)	118.1(3)	H(12*E*)—C(12)—C(8)	117(2)
Fe(2)—C(18)—O(5)	178.1(3)	C(5)—C(9)—C(13)	124.7(3)	H(12*Z*)—C(12)—C(8)	121(2)
Fe(2)—C(19)—O(6)	177.7(4)	C(9)—C(13)—O(1)	122.0(3)	C(13)—C(14)—H(141)	112(2)
Fe(2)—C(20)—O(7)	179.5(4)	C(9)—C(13)—C(14)	119.6(3)	C(13)—C(14)—H(142)	111(2)
		O(1)—C(13)—C(14)	118.2(3)	C(13)—C(14)—H(143)	107(3)

The e.s.d. of the last significant digit is given in parentheses.

TABLE 6

LEAST—SQUARES PLANES IN III

Plane	Atoms defining plane [a]	Equation of mean plane
A	C(1), C(4), C(7), C(8), C(11), C(12)	$-1.018X + 3.624Y + 18.090Z = 6.032$
B	C(18), C(19), a, b	$10.680X - 1.839Y + 0.637Z = 5.418$
C	C(1), C(2), C(3), C(4)	$8.130X + 0.458Y - 10.746Z = 9.458$
D	C(1), C(4), C(5), C(6)	$10.016X - 3.344Y - 7.822Z = 3.841$
E	C(16), C(17), O(3), O(4), Fe(1), c	$2.252X - 5.648Y + 14.006Z = 6.447$
F	O(7), C(20), Fe(2), d, e, f	$3.106X + 8.061Y - 8.005Z = -0.070$

Displacement of atoms from mean plane (Å)

Plane A:	C(1)	0.010	Plane E:	C(16)	0.022	Plane F:	O(7)	0.010
	C(4)	−0.014		C(17)	0.013		C(20)	0.001
	C(7)	0.007		O(3)	−0.011		Fe(2)	−0.022
	C(8)	0.002		O(4)	−0.005		d	0.004
	C(11)	0.007		Fe(1)	−0.023		e	0.009
	C(12)	−0.012		c	0.005		f	−0.001
Plane B:	C(18)	0.014	Plane C:	C(1)	0.001	Plane D:	C(1)	−0.002
	C(19)	−0.015		C(2)	−0.002		C(4)	0.002
	a	0.017		C(3)	0.002		C(5)	−0.003
	b	−0.016		C(4)	−0.001		C(6)	0.003

Dihedral angle between planes (°)

A—B 88.9; A—C 125.2; A—D 116.6; C—D 112.4; D—E 76.7; F—A 89.9; F—B 89.3; F—C 89.9; F—D 89.6; F—E 39.5; E—(Fe(1), C(6), C(10)) 5.0.

[a] a, b, c, d, e and f are the midpoints of the C(7)—C(11), C(8)—C(12), C(6)—C(10), C(7)—C(8), C(2)—C(3) and C(5)—C(6) bonds, respectively.

0.035 gave the positional and thermal parameters listed in Table 3 *. Calculated bond lengths and angles are reported in Tables 4 and 5, respectively. The equations for several least-squares planes and some dihedral angles are presented in Table 6 and a view of the moleculear structure, prepared by the program ORTEP [16], is given in Fig. 1.

The structure consists of discrete monomeric $(C_{12}H_{11}COCH_3)Fe_2(CO)_6$ molecules. The two $Fe(CO)_3$ groups are in *trans* positions with respect to the roof-shaped organic skeleton as in II. The acetylated *s-cis*-butadiene system of the ligand is bonded to Fe(1) through one C—C double bond and the oxygen-atom of the (*Z*)-acetyl substituent. The arrangement of ligands about Fe(1) is trigonal bipyramidal. The three equatorial sites are occupied by 2 CO and the midpoint of C(6)—C(10) (plane E, Table 5) and the C—C double bond makes an angle of 5° with the equatorial plane. The apical sites are occupied by one CO and O(1). The equatorial angles are 127, 127 and 106°, the small angle being that subtended by two Fe—CO bonds. The apical angles are close to 90° (Table 5). H(10*Z*) deviates from the diene plane (plane D, Table 6) away from the metal by 29° and H(10*E*) towards the metal by 25°. The Fe—O(1) bond has a length of 1.997(2) Å, in excellent agreement with the corresponding distance of 1.999(5) Å reported by Sim et al. [17] for the (1-3-η-hexene-5-one)-tricarbonyliron cation. This distance is indicative of an essentially single bond.

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* Lists of observed and calculated structure factors are available on request from R.R.

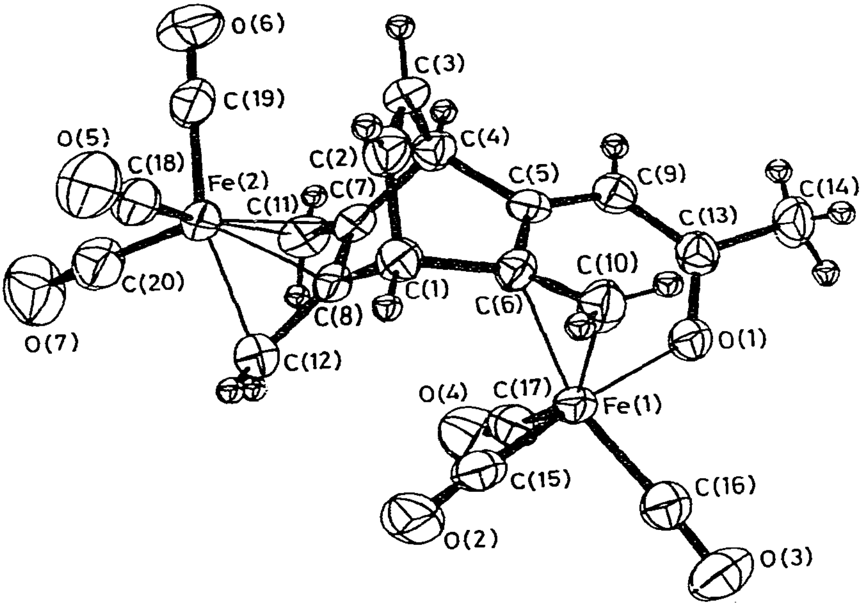


Fig. 1. A perspective view of the molecular structure of $(C_{12}H_{11}COCH_3)Fe_2(CO)_6$ (III).

The Fe—C(15) bond *trans* to the oxygen ligand O(1) is significantly shorter (1.732(3) Å) than the Fe—C(16) and Fe—C(17) bonds "*trans*" to the η^2-C(6)—C(10) ligand (1.800(3) and 1.801(5) Å). This is also in agreement with a negligible back-donation of charge to the oxygen atom O(1). The C(13)—O(1) distance of 1.251(4) Å is longer than the corresponding distance reported by Sim et al. [17] and the mean CO distance of 1.215(5) Å reported for ketones and aldehydes [18]. Thus, the acyl CO bond order appears to be affected by the formation of the Fe—O(1) bond. This is in agreement with the ν(CO) at 1590 cm^{-1}, whereas normal ketone absorption is at ca. 1710 cm^{-1}, and brings further support to the right limit structure presented in Scheme 2.

The arrangement of ligands about Fe(2) is approximately tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints a and b of the *exo* C—C bonds of one *s-cis*-butadiene system, a—b—C(18)—C(19) defining the basal plane (plane B, Table 6). The apex-to-base angles are 100° for the carbonyl groups and 115° for the C—C bond midpoints. The basal angles are 95, 86 and 69°, the small angle being that subtended by the two outer C—C bonds of the diene. The diene is perpendicular to the basal plane, the distance Fe(1)—plane is 0.53 Å. The three C—C bond lengths of the diene are equal within experimental errors. The sum of angles at the "inner" carbon atoms C(7) and C(8) is 360.0(3)°. In contrast, H(*Z*) atoms deviate from the diene plane (plane A, Table 6) away from Fe(2) by 40° and H(*E*) atoms deviate towards the metal by 10°. These values are in agreement with the mean deviations found from a comparison of other (1,3-diene)$Fe(CO)_3$ structures [19].

Diene—heterotriene tricarbonyliron coordination equilibrium in solution

The red crystals of III turn yellow-orange on melting. A solution of III in degassed CD_2Cl_2 experiences the same color change upon standing a few hours at 40° C. Its ^1H NMR spectrum showed a gradual decrease in the intensities of three signals characteristic of III (the H(9) singlet at 6.12 ppm, and the two H(10*E*) and H(10*Z*) doublets at 3.67 and 0.92 ppm), and a corresponding increase in the intensities of three new signals, i.e. a singlet and two doublets at 3.60, 2.55 and 1.66 ppm respectively. The geminal coupling constant $J(E—Z)$ increased from 2.4 to 3.2 Hz for the doublets of the new species. The latter value is the same as that found for II [1] and suggests the same tetrahapto mode of bonding for C(5, 6, 9, 10) as in II. Chromatography of the yellow-orange solution gave III (red, 2%) and complex IV (yellow, 98%) whose analytical data (Experimental) are in agreement with those of an isomer of III. The NMR data of IV (Table 1) indicate that H(9) and C(9) are much more shielded than in III while the C(5—8) chemical shifts are quite similar to those of II. The two tetrahaptotricarbonyliron groups are now bonded to the two *cis*-butadiene systems as in II, leaving the keto group uncoordinated (Scheme 1). One coordination site of Fe(1) has thus shifted from the keto group to the second exocyclic double bond C(5)—C(9) of the acetylated butadiene system.

The III → IV process corresponds to the isomerisation of a trigonal bipyramidal (heterotriene)$Fe(CO)_3$ to a tetragonal pyramidal (1,3-diene)$Fe(CO)_3$ system. This process is reversible since the same ^1H NMR spectrum was observed when equilibrating III or IV in CD_2Cl_2 at the same temperature. The thermodynamic and kinetic parameters of equilibrium III ⇌ IV in dichloromethane were determined by UV spectrophotometry (Experimental) and are presented in Table 7. The III → IV process is exothermic, thus III is the kinetically favoured product of the Friedel-Crafts acetylation of II and IV the thermodynamically stable isomer. III most probably arises by proton loss from the expected allyl-$Fe(CO)_3$ cationic intermediate i which is analogous to the (1-acetylbutadienyl)-tricarbonyliron cation reported by Knox et al. [6] (Scheme 3).

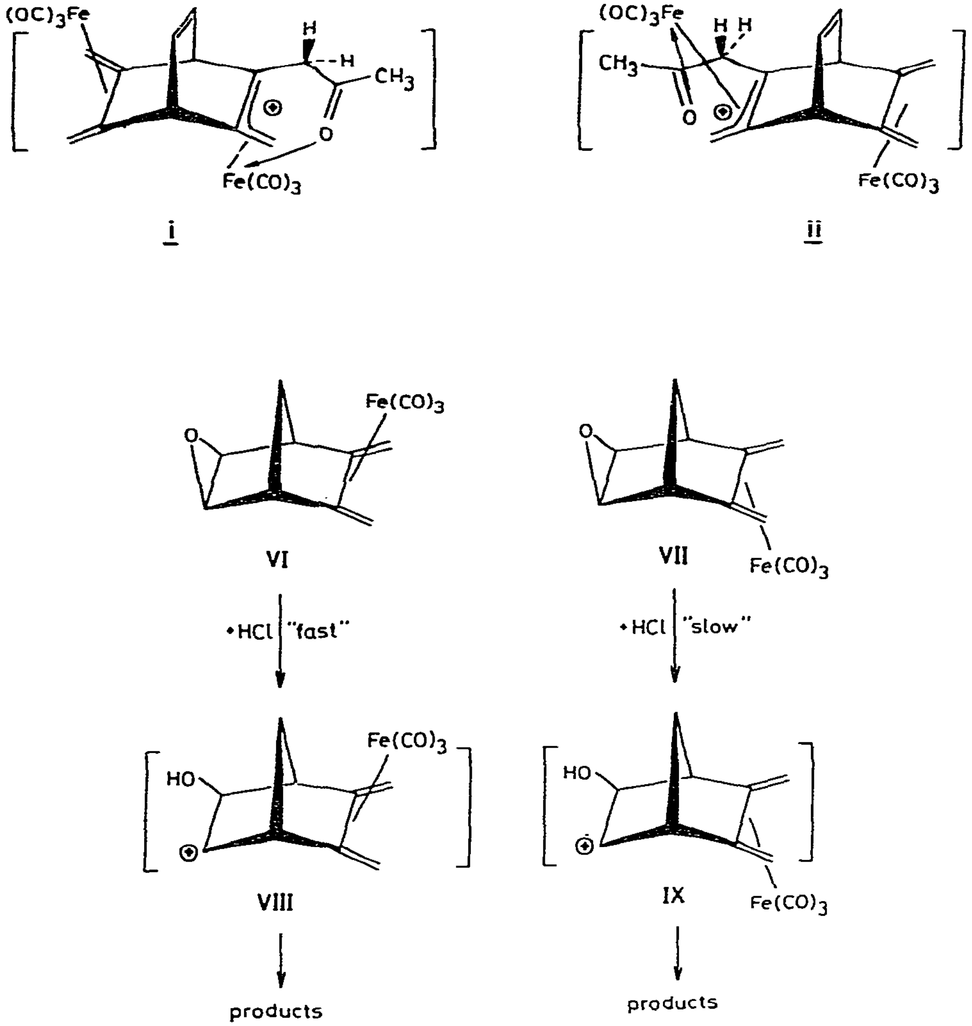
The isomerisation goes by an intramolecular mechanism since the rate of approach to equilibrium ($k_1 + k_{-1}$) is independent of the concentration of the

TABLE 7

THERMODYNAMIC AND KINETIC PARAMETERS FOR THE EQUILIBRIUM III ⇌ IV IN DICHLOROMETHANE

ΔT studied [a] (K)	K_{293} [b]	ΔG_{293} (kcal/mol)	ΔH [c] (kcal/mol)	ΔS [d] (e.u.)
283—313	101 ± 2	—2.7 ± 0.1	—4.0 ± 0.2	—4 ± 1
ΔT studied [a] (K)	$k_1 \times 10^5$ [e] (s^{-1})	$\Delta G^{\ddagger}_{1}$ [f] (kcal/mol)	$\Delta H^{\ddagger}_{1}$ [g] (kcal/mol)	$\Delta S^{\ddagger}_{1}$ (e.u.)
283—313	2.0 ± 0.1	23.4 ± 0.1	22.0 ± 0.7	—5 ± 2

[a] ±0.1 K; [b] $K = [IV]/[III] = k_1/k_{-1}$; [c] Calculated from the slope of ln K vs. T^{-1} (6 points, alignment coefficient bb′ = 0.9988); [d] Slope of $RT\ln K$ vs. T (bb′ = 0.998); [e] At 293 K; calculated from the slope of $\ln(A_t - A_\infty)$ vx. t (λ = 525 nm, bb′ = 0.9999) and K_{293}; [f] at 293 K; $\Delta G^* = [\ln(k_B/h) - \ln(k/T)]RT$; [g] Calculated from the slope of $\ln(k_1/T)$ vs. T^{-1} (8 points, bb′ = 0.9989). The measurements are: (T °C, ($k_1 + k_{-1}$) × 10^6 s^{-1}, K) (10, 4.91 ± 0.04, 130 ± 3) (20, 20.91 ± 0.04, 102 ± 4) (31, 88.7 ± 0.3, 80 ± 3) (40, 259 ± 6, 66 ± 2) (45, 481 ± 2, 59 ± 2) (48, 614 ± 15, 56 ± 2) (54, 1070 ± 20, 50 ± 1) (58, 1768 ± 7, 46 ± 1).



SCHEME 3

starting complex. Since both $\Delta S^*_{k_1}$ and $\Delta S^*_{k_{-1}}$ are close to zero, the main contribution to the ΔG^*'s is enthalpic (e.g. $T\,\Delta S^*_{k_1}$ contributes only 6% to $\Delta G^*_{k_1}$ at 293 K). Several factors contribute to $\Delta H^*_{k_1}$. Of these, the enthalpy of activation required for the fluxional change between a tetragonal pyramidal and a trigonal bipyramidal geometry is probably minor, since the intramolecular CO exchange in IV was found by ^{13}C NMR to be blocked at ca. −40°C. A full discussion of the contribution of other factors (e.g. the ΔH^* of solvation) must await other examples of such a coordination equilibrium.

The *Z*/*E* isomerisation of IV requires a much higher energy of activation. It was observed only upon heating crystals of IV under argon at 170°C for 5 min. Chromatography of the product brought down III (2%) and complex V (98%) (Scheme 1) which is an isomer of IV (Experimental). Its NMR data (Table 1) show unambiguously a H(9) signal in the H(Z) region (highfield shift of 2.50 ppm with respect to IV), the acetyl substituent being thus in the E position. The keto group (ν(C=O) 1667 cm^{-1}) is uncoordinated since the C(5, 6, 9, 10) chemical shifts and J(H(10E),H(10Z)) are typical of a 1,3-diene coordinated to a tetrahaptotricarbonyliron group.

This study provides a route to Z or E monoacetylated derivatives of the pentaene I by stereospecific Friedel-Crafts acylation of an unsymmetrically bimetallated complex. The preference of the Friedel-Crafts electrophile (AcCl/$AlCl_3$) for the attack onto the *endo*-(diene)$Fe(CO)_3$ contrasts strikingly with the stereoselective protonation of the *exo*-(diene)$Fe(CO)_3$ of II by HCl/$AlCl_3$. We had shown [2] that the endocyclic double bond in II coordinates to the (allyl)$Fe(CO)_3$ cation generated upon protonation. Obviously, this is possible only for the protonated *exo*-(diene)$Fe(CO)_3$ system. The present work demonstrates that the intervention of the endocyclic double bond is not required in the case of the Friedel-Crafts acetylation of II, since the (acetylmethyl)allylFe-$(CO)_3$ cation generated upon addition of $CH_3CO^+AlCl_4^-$ is coordinatively saturated by the dative $CH_3CO\cdots Fe$ bond (cf. i). This does not explain yet why the acetylation of the *exo*-(diene)$Fe(CO)_3$ of II is not competitive. We propose the following interpretation.

The $Fe(CO)_3$ group plays the role of a $-I$ substituent [20]. This was confirmed by the study of S_N1 solvolyses of esters remotely perturbed by (diene)-$Fe(CO)_3$ groups [4]. We have reported [21] that the acid-promoted epoxide ring opening of the *exo* complex VI is much faster than that of its *endo* isomer VII (Scheme 3) under the same conditions, probably because the $-I$ effect of the *endo*-$Fe(CO)_3$ destablizes more the cationic intermediate IX than the *exo*-Fe-$(CO)_3$ group in VIII. The stereoselectivity of the acetylation of II is probably governed by the relative stability of the cationic intermediates i and ii. Similarly to VIII and IX, i is expected to be more stable than ii because of a smaller destabilizing effect by the *exo*-(diene)$Fe(CO)_3$ in i than by the *endo*-$Fe(CO)_3$ group in ii (the possible participation of the endocyclic double bond to the positive charge delocalization [22] is not expected to be significant because i and ii are already strongly delocalized cations).

Experimental

All reactions were carried out under argon and the solvents were purified, dried and degassed by standard methods [23]. Mass spectra at 70 eV were measured with a Hewlett-Packard GC-MS 5980; IR spectra in n-hexane and in KBr pellets with a Perkin-Elmer 577 spectrophotometer; UV spectra in n-heptane with a Beckman Acta V spectrophotometer; ^{1}H NMR spectra with a Bruker WP-80 and a Bruker WP-60 spectrometer in the CW and the FT modes, respectively; ^{13}C NMR spectra with a Bruker WP-60 instrument (15.08 MHz) in the FT mode and using a deuterium lock. The melting points (uncorrected) were measured with a Tottoli apparatus. E. Manzer (Mikrolabor, ETH, Zürich) carried out the microanalyses. The preparations of I and II have been described elsewhere [24,1].

Preparation of complexes

a) A mixture of freshly sublimed $AlCl_3$ (0.155 g; 1.16 mmol) and CH_3COCl (0.091 g; 1.16 mmol) in dichloromethane (2 ml) was added dropwise to a stirred solution of complex II (0.5 g; 1.147 mmol) in dichloromethane (30 ml) at 0°C. After 5 min the red solution was quenched at 0°C by vigorous stirring in saturated aqueous $NaHCO_3$/MeOH (1 : 1) (200 ml). The mixture was extracted with dichloromethane (100 ml) and the organic phase dried over $MgSO_4$ and chromatographed on a 30 × 2 cm column packed with silica gel. Elution with CH_2Cl_2/n-hexane (1 : 1) gave a single red band (TLC R_f ~0.8) which yielded complex III (0.315 g; 0.659 mmol; 57.5%) * after recrystallisation from n-hexane at −25°C.

III: red crystals (single crystals for the X-ray measurements were obtained by slow cooling to −25°C of a saturated solution in n-hexane), m.p. 115–116°C (melting is accompanied with isomerisation to complex IV). Analysis. Found: C, 50.73; H, 3.04. $C_{20}H_{14}O_7Fe_2$ calcd.: C, 50.25; H, 2.95%. Mass spectrum, *m/e*: 478 (M^+; <0.1), 450 (23), 422 (54), 394 (49), 366 (12), 338 (22), 310 (100) (successive losses of 6 CO), 284 (24), 198 (47), 184 (47), 155 (56), 56 (Fe^+). IR (n-hexane): ν(CO) 2060, 1982, 1973 and 1965 cm^{-1}; ν(C=O) 1590 cm^{-1} (in KBr). UV spectrum, λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 475 (1460), 336(sh) (5810), 300(sh) (10 800), 278 (15 200).

b) A glass tube containing a solution of III (0.1 g) in dichloromethane (8 ml) was sealed on a vacuum line and then heated at 55°C for 10 min. The red solution turned yellow-orange and was shown by ^1H NMR to contain a mixture of complexes III and IV (molar ratio 2 : 98, which decreased slightly on cooling). Chromatography on silica gel with CH_2Cl_2/n-hexane (1 : 1) gave complex III, then elution with pure CH_2Cl_2 brought down a single yellow band which yielded complex IV (TLC R_f ~0.5, CH_2Cl_2) after crystallisation from n-hexane at −25°C. Yield 97%.

IV: yellow crystals, m.p. 115°C (identical melt to that obtained with III). Analysis. Found: C, 50.80; H, 3.11. $C_{20}H_{14}O_7Fe_2$ calcd.: C, 50.25; H, 2.95%. Mass spectrum: 478 (M^+; 0.4), 450 (15), 422 (54), 394 (35), 366 (12), 338 (17), 310 (100) (successive losses of 6 CO), 284 (20), 198 (15), 184 (17), 155 (17), 128 (30), 112 (39), 84 (22), 56 (Fe^+). IR (n-hexane): ν(CO) 2062, 1994, 1987 and 1976 cm^{-1}; ν(C=O) 1680 cm^{-1} (in KBr). UV spectrum: 300(sh) (5990), 220(sh) (41 300).

c) A glass tube containing complex IV (0.1 g) was sealed under argon (1 atm) and heated in an oil bath at 170°C for 5 min. After cooling, the yellow solid was chromatographed on a 20 × 2 cm column packed with silica gel. Elution with CH_2Cl_2/n-hexane (1 : 1) gave a red band containing traces of III, then a yellow band which yielded complex V (TLC R_f ~0.5, CH_2Cl_2/n-hexane (1 : 1)) after crystallisation from n-hexane at −25°C. Yield 98%.

V: yellow crystals, m.p. 165°C. Analysis. Found: C, 50.91; H, 3.28. $C_{20}H_{14}O_7Fe_2$ calcd.: C, 50.25; H, 2.95%. Mass spectrum, *m/e*: 478 (M^+; 0.1), 450 (7), 422 (44), 394 (39), 366 (6), 338 (9), 310 (100) (successive losses of 6 CO), 284 (21), 198 (17), 184 (18), 155 (18), 128 (20), 112 (29), 84 (19), 56 (Fe^+).

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* Optimisation of yields was not attempted.

IR (n-hexane): ν(CO) 2076, 2063, 2001, 1986 and 1973 cm^{-1}; ν(C=O) 1667 cm^{-1} (in KBr).

Kinetic measurements

a) Known amounts of IV were dissolved in degassed dichloromethane (dried over neutral alumina, grade I) (c_{IV} 1—3 × 10^{-2} *M*) in thermostated quartz cells and the temperature of the solution was measured with a thermistor. The absorbance at 525 nm was measured at equilibrium and the equilibrium constant K = [IV]/[III] calculated by solving the simultaneous equations [III] + [IV] = c_{IV} and ϵ_{III}[III] + ϵ_{IV}[IV] = A_{525}. At 525 nm the difference in ϵ's is greatest (ϵ_{III} 1310, ϵ_{IV} 50 M^{-1} cm^{-1}) and the contributions of both chromophores to A_{525} is of the same order of magnitude (e.g. at 40°C: c_{IV} 1.52 × 10^{-2} *M*, A_{525} = 0.361 and ϵ_{IV}[IV] contributes 21% to the total absorbance). The results were then checked by approaching the equilibrium from the other side (starting with pure III).

b) Thermostatted quartz cells equipped with a thermistor were filled with a solution of III (c_{III} 1—5 × 10^{-4} *M*) in dry and degassed dichloromethane and hermetically closed. The absorbance was followed at 525 nm to 60—80% of the approach to the position of equilibrium III $\rightleftharpoons$ IV. For such an equilibrium, $-\ln([\mathrm{III}]_t - [\mathrm{III}]_{eq}) + \ln(c_{III} - [\mathrm{III}]_{eq}) = (k_1 + k_{-1})t$, and the slope of $\ln(A_t - A_\infty)$ vs. t gives $(k_1 + k_{-1})$. Knowing $K = k_1/k_{-1}$, k_1 and k_{-1} were calculated for each temperature and the activation parameters computed by the program RELICI [25] (Table 7).

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