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REGIOSELECTIVE ADDITION OF PROTIC ACIDS TO TRICARBONYLIRON COMPLEXES OF 2,3,5,6-TETRAKIS(METHYLENE)-7-OXABICYCLO[2.2.1]HEPTANE. CRYSTAL STRUCTURE OF $(C_{10}H_{10}O)Fe_2(CO)_6$

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Summary

The main product of the thermal reaction between the title oxatetraene (I) and $Fe_2(CO)_9$ in ether/pentane is the bimetallic complex $(C_{10}H_{10}O)Fe_2(CO)_6$-*diexo* (II), which has C_{2v} symmetry both in the solid state (X-ray analysis) and in solution. Whereas the protonation of the free ligand leads usually to polymerisation, the addition of a protic acid such as CF_3CO_2H to II proceeds cleanly at 0° C giving first a $(\eta^3\text{-allyl})Fe(CO)_3O_2CCF_3$ complex (III). The intermediate III adds a second equivalent of acid in a slower step ($k_2/k_1 = 0.1$, $CF_3CO_2D/CHCl_3$, 0° C) giving the *trans*-bis(η^3-allyl) isomer IV with high regioselectivity. The addition of CF_3CO_2D yields the corresponding deuteriomethylallyliron tricarbonyl trifluoroacetates III′ and IV′. No further deuterium incorporation is observed at 0° C, thus confirming the kinetic control of the regioselective double addition of protic acid to II.

Introduction

The oxatetraene 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane (I, Scheme 1) has recently proved to be an important synthon for the preparation

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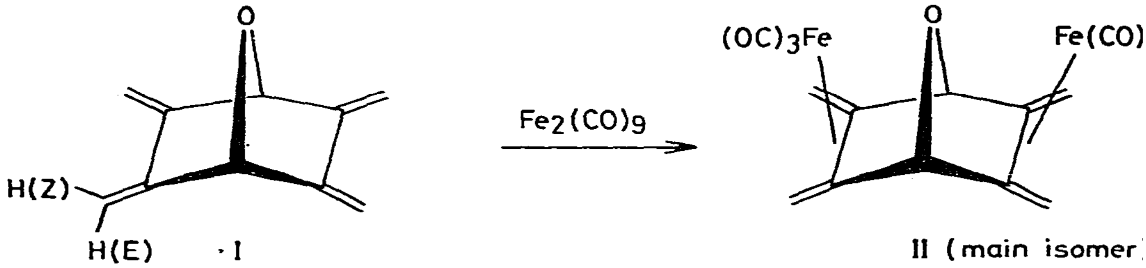
SCHEME 1



of antitumoral anthracyclines [1]. As the stereoselective addition of electrophiles to I should be facilitated by prior coordination of its two *s-cis*-butadiene systems to a metal, we have prepared a series of iron carbonyl complexes of I [2,3] in order to examine their reactivity. The main product of the thermal reaction between I and $Fe_2(CO)_9$ in ether/n-pentane is the bimetallic complex $(C_{10}H_{10}O)Fe_2(CO)_6$-*diexo* (II, Scheme 1) which was shown by ^1H and ^{13}C NMR to have C_{2v} symmetry in solution and to be inert towards epimerisation in the presence of traces of acids or iron carbonyls. We report here a kinetic study of the addition of a protic acid, CF_3CO_2D, to II, as well as a crystal structure determination of this bimetallic complex to confirm the stereochemical conclusions.

Crystal structure of $(C_{10}H_{10}O)Fe_2(CO)_6$

X-Ray measurements were carried out with a Syntex $P2_1$ automatic four-circle diffractometer; the crystal data and methods used are summarised in Table 1. The crystal form was accurately measured as before [5] and used to

TABLE 1

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

Formula	$(C_{10}H_{10}O)Fe_2(CO)_6$ $C_{16}H_{10}O_7Fe_2$	Radiaton	Mo-K_α, Nb filtered $\lambda = 0.71069$ Å
Mol. weight	425.95	μ (cm^{-1})	18.4
Dimensions (mm)	0.09 × 0.12 × 0.15	Scan method	2θ—θ
Crystal class	Triclinic	Background from	Scan profile interpretation [4]
a (Å)	8.870(2)		
b (Å)	9.645(1)	$(\sin\theta/\lambda)_{max}$	0.54
c (Å)	9.911(1)	Data collected	$+h, \pm k, \pm l$
α (deg)	79.69(2)	No. of unique reflections	2188
β (deg)	83.12(3)	No. of reflections $<3\sigma$	641
γ (deg)	85.97(3)	No. of observations/No. of variables	8.2
V (Å^3)	827.2		
Z	2	Structure solution	Patterson and Fourier
d_{calcd} (g/cm^3)	1.71	Refinement method	Block diagonal least-squares
$d_{obsd.}$ (g/cm^3)	1.72(1)	Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
F_{000}	428	w	$1/\sigma^2$
Space group	$P\bar{1}$	R	0.027
		R_w	0.024
		Goodness of fit	1.38

TABLE 2

ATOMIC COORDINATES AND THERMAL PARAMETERS (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

Atom	X	Y	Z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.6762(4)	−0.0074(4)	0.1904(3)	0.030(2)	0.034(2)	0.029(2)	−0.002(2)	−0.006(2)	−0.009(2)
C(2)	0.5898(4)	0.0852(3)	0.2888(3)	0.028(2)	0.026(2)	0.033(2)	0.001(2)	0.000(2)	−0.003(2)
C(3)	0.7062(4)	0.1464(3)	0.3401(3)	0.031(2)	0.027(2)	0.028(2)	0.003(2)	−0.005(2)	−0.005(2)
C(4)	0.8538(4)	0.0843(4)	0.2723(3)	0.030(2)	0.031(2)	0.031(2)	−0.005(2)	−0.007(2)	−0.004(2)
C(5)	0.8597(4)	−0.0710(3)	0.3415(3)	0.036(2)	0.029(2)	0.022(2)	0.008(2)	−0.002(2)	−0.005(2)
C(6)	0.7440(4)	−0.1309(3)	0.2886(3)	0.031(2)	0.024(2)	0.030(2)	0.001(2)	−0.001(2)	−0.007(2)
C(8)	0.4364(4)	0.1236(4)	0.3236(4)	0.040(3)	0.041(2)	0.040(3)	−0.003(2)	0.000(2)	−0.006(2)
C(9)	0.6709(5)	0.2466(4)	0.4261(4)	0.038(3)	0.039(3)	0.048(3)	0.003(2)	−0.007(2)	−0.014(2)
C(10)	0.9527(5)	−0.1572(4)	0.4319(4)	0.055(3)	0.037(3)	0.034(2)	0.005(2)	−0.011(2)	−0.009(2)
C(11)	0.7204(5)	−0.2756(4)	0.3231(4)	0.046(3)	0.033(2)	0.036(3)	−0.005(2)	0.001(2)	−0.004(2)
C(12)	0.4996(5)	0.2966(4)	0.0764(4)	0.047(3)	0.045(2)	0.052(3)	0.003(2)	−0.014(2)	−0.003(2)
C(13)	0.7279(5)	0.3953(4)	0.1445(4)	0.049(3)	0.032(2)	0.051(3)	0.007(2)	−0.009(2)	−0.010(2)
C(14)	0.4488(5)	0.4363(4)	0.2999(4)	0.044(3)	0.040(3)	0.061(3)	0.001(2)	−0.004(2)	−0.004(2)
C(15)	1.0067(5)	−0.4134(4)	0.2969(4)	0.054(3)	0.045(3)	0.048(3)	0.005(2)	−0.008(2)	−0.010(2)
C(16)	0.9141(4)	−0.2297(4)	0.0683(4)	0.035(2)	0.032(2)	0.047(3)	−0.004(2)	0.006(2)	−0.007(2)
C(17)	1.1328(5)	−0.1591(4)	0.1884(4)	0.056(3)	0.043(3)	0.039(2)	0.001(2)	−0.002(2)	−0.012(2)
Fe(1)	0.56908(6)	0.29987(5)	0.23644(5)	0.0357(3)	0.0297(3)	0.0401(3)	0.0024(2)	−0.0050(3)	−0.0047(2)
Fe(2)	0.95070(6)	−0.23222(5)	0.24369(5)	0.0396(3)	0.0296(3)	0.0343(3)	0.0034(2)	−0.0031(3)	−0.0061(2)
O(1)	0.4569(4)	0.2928(3)	−0.0272(3)	0.082(2)	0.095(2)	0.056(2)	0.002(2)	−0.031(2)	−0.009(2)
O(2)	0.8269(3)	0.4524(3)	0.0799(3)	0.059(2)	0.056(2)	0.098(3)	−0.018(2)	0.016(2)	−0.005(2)
O(3)	0.3757(3)	0.5240(3)	0.3436(3)	0.068(2)	0.056(2)	0.102(2)	0.015(2)	0.009(2)	−0.026(2)
O(4)	1.0341(4)	−0.5317(3)	0.3321(3)	0.093(3)	0.037(2)	0.107(3)	0.017(2)	−0.018(2)	0.004(2)
O(5)	0.8883(3)	−0.2246(3)	−0.0422(3)	0.059(2)	0.075(2)	0.034(2)	−0.014(2)	−0.003(2)	−0.012(2)
O(6)	1.2495(3)	−0.1134(3)	0.1610(3)	0.050(2)	0.095(2)	0.066(2)	−0.023(2)	0.001(2)	−0.019(2)
O(7)	0.8086(2)	0.0726(2)	0.1392(2)	0.032(1)	0.034(1)	0.025(1)	−0.004(1)	−0.001(1)	−0.003(1)
H(1)	0.625(3)	−0.032(3)	0.119(3)	0.033(9(					
H(4)	0.944(3)	0.136(3)	0.260(3)	0.018(7)					
H(8*E*)	0.353(4)	0.097(3)	0.265(3)	0.04(1)					
H(8*Z*)	0.411(3)	0.136(3)	0.411(3)	0.016(9)					
H(9*E*)	0.743(4)	0.302(3)	0.440(3)	0.03(1)					
H(9*Z*)	0.580(4)	0.235(3)	0.486(3)	0.05(1)					
H(10*E*)	1.043(4)	−0.117(3)	0.453(3)	0.04(1)					
H(10*Z*)	0.907(4)	−0.224(3)	0.499(3)	0.04(1)					
H(11*E*)	0.662(4)	−0.314(3)	0.267(3)	0.04(1)					
H(11*Z*)	0.730(4)	−0.316(3)	0.413(3)	0.05(1)					

TABLE 3

BOND LENGTHS (Å) IN II (the e.s.d. of the last significant digit is given in parentheses)

Fe(1)—C(2)	2.044(3)	Fe(2)—C(5)	2.046(3)
Fe(1)—C(3)	2.056(3)	Fe(2)—C(6)	2.055(3)
Fe(1)—C(8)	2.130(4)	Fe(2)—C(10)	2.120(4)
Fe(1)—C(9)	2.147(4)	Fe(2)—C(11)	2.142(4)
Fe(1)—C(12)	1.776(5)	Fe(2)—C(15)	1.786(5)
Fe(1)—C(13)	1.799(4)	Fe(2)—C(16)	1.802(4)
Fe(1)—C(14)	1.790(4)	Fe(2)—C(17)	1.793(4)
C(12)—O(1)	1.143(6)	C(15)—O(4)	1.150(5)
C(13)—O(2)	1.137(5)	C(16)—O(5)	1.137(5)
C(14)—O(3)	1.145(5)	C(17)—O(6)	1.137(5)
C(1)—C(2)	1.540(5)	C(4)—C(3)	1.533(5)
C(1)—C(6)	1.533(4)	C(4)—C(5)	1.532(4)
C(1)—O(7)	1.441(4)	C(4)—O(7)	1.449(4)
C(2)—C(3)	1.412(5)	C(5)—C(6)	1.408(5)
C(2)—C(8)	1.404(5)	C(5)—C(10)	1.410(5)
C(3)—C(9)	1.395(6)	C(6)—C(11)	1.401(5)
C(1)—H(1)	0.96(3)	C(4)—H(4)	0.95(3)
C(8)—H(8*E*)	1.07(3)	C(10)—H(10*E*)	0.97(3)
C(8)—H(8*Z*)	0.90(3)	C(10)—H(10*Z*)	0.92(3)
C(9)—H(9*E*)	0.90(3)	C(11)—H(11*E*)	0.94(4)
C(9)—H(9*Z*)	0.94(3)	C(11)—H(11*Z*)	0.92(3)

TABLE 4

BOND ANGLES (°) IN II (the e.s.d. of the last significant digit is given in parentheses)

C(2)—Fe(1)—C(8)	39.2(1)	C(5)—Fe(2)—C(10)	39.5(1)
C(2)—Fe(1)—C(3)	40.3(1)	C(5)—Fe(2)—C(6)	40.2(1)
C(3)—Fe(1)—C(9)	38.7(1)	C(6)—Fe(2)—C(11)	38.9(1)
C(12)—Fe(1)—C(14)	101.9(2)	C(15)—Fe(2)—C(16)	101.8(2)
C(13)—Fe(1)—C(14)	102.4(2)	C(15)—Fe(2)—C(17)	100.5(2)
C(12)—Fe(1)—C(13)	89.1(2)	C(16)—Fe(2)—C(17)	91.9(2)
Fe(1)—C(12)—O(1)	178.8(3)	Fe(2)—C(15)—O(4)	176.1(4)
Fe(1)—C(13)—O(2)	176.0(4)	Fe(2)—C(16)—O(5)	178.0(3)
Fe(1)—C(14)—O(3)	177.5(4)	Fe(2)—C(17)—O(6)	176.1(4)
C(2)—C(1)—C(6)	103.4(3)	C(3)—C(4)—C(5)	104.2(3)
C(2)—C(1)—O(7)	101.3(3)	C(3)—C(4)—O(7)	100.8(3)
C(6)—C(1)—O(7)	101.3(3)	C(5)—C(4)—O(7)	100.8(3)
C(1)—C(2)—C(3)	103.9(3)	C(4)—C(5)—C(6)	104.5(3)
C(1)—C(2)—C(8)	135.3(3)	C(4)—C(5)—C(10)	135.6(4)
C(3)—C(2)—C(8)	120.6(3)	C(6)—C(5)—C(10)	119.8(3)
C(2)—C(3)—C(4)	104.4(3)	C(1)—C(6)—C(5)	104.0(3)
C(4)—C(3)—C(9)	134.9(4)	C(1)—C(6)—C(11)	134.8(3)
C(2)—C(3)—C(9)	120.6(3)	C(5)—C(6)—C(11)	121.1(3)
C(1)—O(7)—C(4)	96.9(2)		
H(1)—C(1)—C(2)	119(2)	H(4)—C(4)—C(3)	119(2)
H(1)—C(1)—C(6)	116(2)	H(4)—C(3)—C(5)	119(2)
H(1)—C(1)—O(7)	113(2)	H(4)—C(4)—O(7)	110(2)
H(8*E*)—C(8)—H(8*Z*)	120(2)	H(10*E*)—C(10)—H(10*Z*)	117(3)
H(8*E*)—C(8)—C(2)	119(2)	H(10*E*)—C(10)—C(5)	118(2)
H(8*Z*)—C(8)—C(2)	116(2)	H(10*Z*)—C(10)—C(5)	118(2)
H(9*E*)—C(9)—C(9*Z*)	122(3)	H(11*E*)—C(11)—H(11*Z*)	123(3)
H(9*E*)—C(9)—C(3)	120(2)	H(11E)—C(11)—C(6)	117(2)
H(9*Z*)—C(9)—C(3)	116(2)	H(11*Z*)—C(11)—C(6)	116(2)

TABLE 5

LEAST-SQUARES PLANES OF II

Plane	Atoms defining plane [a]	Equation of mean plane
I	O(3), C(14), Fe(1), O(7), Fe(2), C(15), O(4)	$7.191X + 4.630Y + 5.592Z = 6.950$
II	H(1), C(1), O(7), C(4), H(4)	$-4.512X + 7.938Y + 0.786Z = -2.969$
III	C(1), C(2), C(3), C(4)	$0.365X - 6.223Y + 6.306Z = 1.499$
IV	C(2), C(3), C(8), C(9)	$0.077X - 5.770Y + 6.744Z = 1.503$
V	C(12), C(13), a, b	$-4.783X + 6.388Y + 5.058Z = -0.168$
VI	C(1), C(4), C(5), C(6)	$-4.908X + 3.054Y + 7.244Z = -1.962$
VII	C(5), C(6), C(10), C(11)	$-4.801X + 2.593Y + 7.463Z = -1.761$
VIII	C(16), C(17), c, d	$-1.753X + 8.302Y - 2.998Z = -3.792$

Displacement of atoms from mean plane (Å)

Plane	O(3)	0.099	Fe(2)	0.174	Plane	H(1)	−0.010	Plane	C(1)	−0.005
I	C(14)	−0.025	C(15)	0.036	II	C(1)	0.008	III	C(2)	0.007
	Fe(1)	−0.147	O(4)	−0.118		O(7)	0.006		C(3)	−0.007
	O(7)	−0.020				C(4)	0.000		C(4)	0.005
						H(4)	−0.005			
Plane	C(2)	−0.001			Plane	C(12)	0.060	Plane	C(1)	−0.001
IV	C(3)	0.001			V	C(13)	−0.057	VI	C(4)	0.001
	C(8)	0.000				a	0.068		C(5)	−0.001
	C(9)	0.000				b	−0.070		C(6)	0.001
Plane	C(5)	−0.003			Plane	C(16)	0.078			
VII	C(6)	0.003			VIII	C(17)	−0.080			
	C(10)	0.001				c	0.097			
	C(11)	−0.001				d	−0.096			

Dihedral angle between planes (°)

I—II 87.1; I—III 86.3; I—IV 85.7; I—V 87.2; I—VI 89.6; I—VII 89.6; I—VIII 88.0;
II—III 125.8; II—VI 125.7; III—IV 4.1; III—VI 108.5; IV—V 86.9; VI—VII 3.3; VII—VIII 88.1

[a] a, b, c, d are the midpoints of the C(2)—C(8), C(3)—C(9), C(5)—C(10) and C(6)—C(11) bonds, respectively.

correct the intensities for absorption. The computer programs used for the data reduction and structure analysis were taken from the "X-RAY 72" program system [6]. Scattering factors for the neutral non-hydrogen atoms were taken from Cromer and Mann [7] and for hydrogen atoms from Stewart et al. [8]. Anomalous dispersion coefficients for Fe were taken from Cromer [9]. The structure was solved by Patterson and Fourier methods. Hydrogen atoms were located after refinement to $R = 0.042$, and refinement continued to $R = 0.027$. The perspective drawing was prepared by the ORTEP program [10]. The final positional and thermal parameters are listed in Table 2. Calculated bond lengths and angles are reported in Tables 3 and 4, respectively. * The equations for several least-squares planes and some dihedral angles are presented in Table 5. A view of the molecular structure is given in Fig. 1, where the numbering scheme is indicated. For the $C_{10}H_{10}O$ ligand, the numbering scheme is identical with that used for nomenclature purposes.

The structure is composed of discrete monomeric $(C_{10}H_{10}O)Fe_2(CO)_6$ molecules. The complex has a C_{2v} symmetry, with the two perpendicular mirror planes passing through the iron atoms, two CO groups and O(7) (plane I), and through the bridgehead carbon atoms and O(7) (plane II, Table 5). The

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* Tables of observed and calculated structure factors can be obtained from the authors.

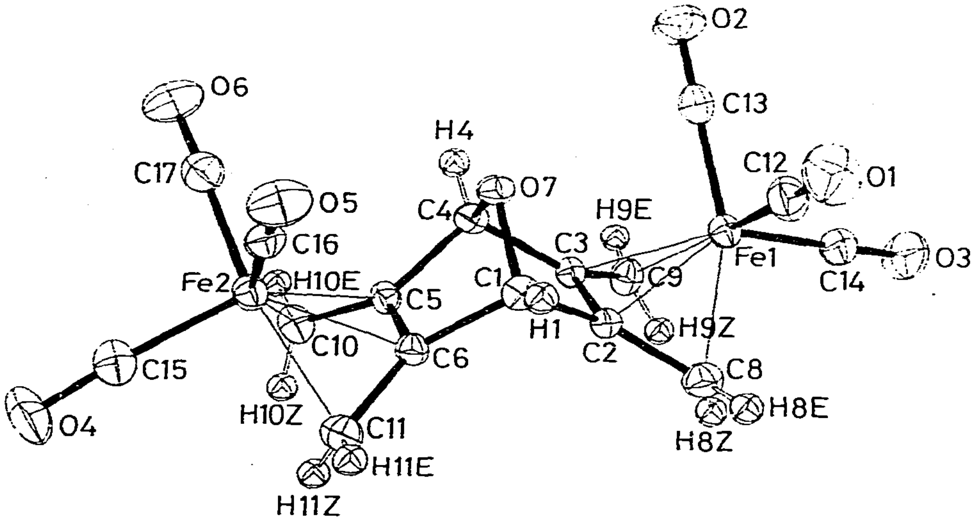


Fig. 1. A perspective view of the molecular structure of $(C_{10}H_{10}O)Fe_2(CO)_6$ (II).

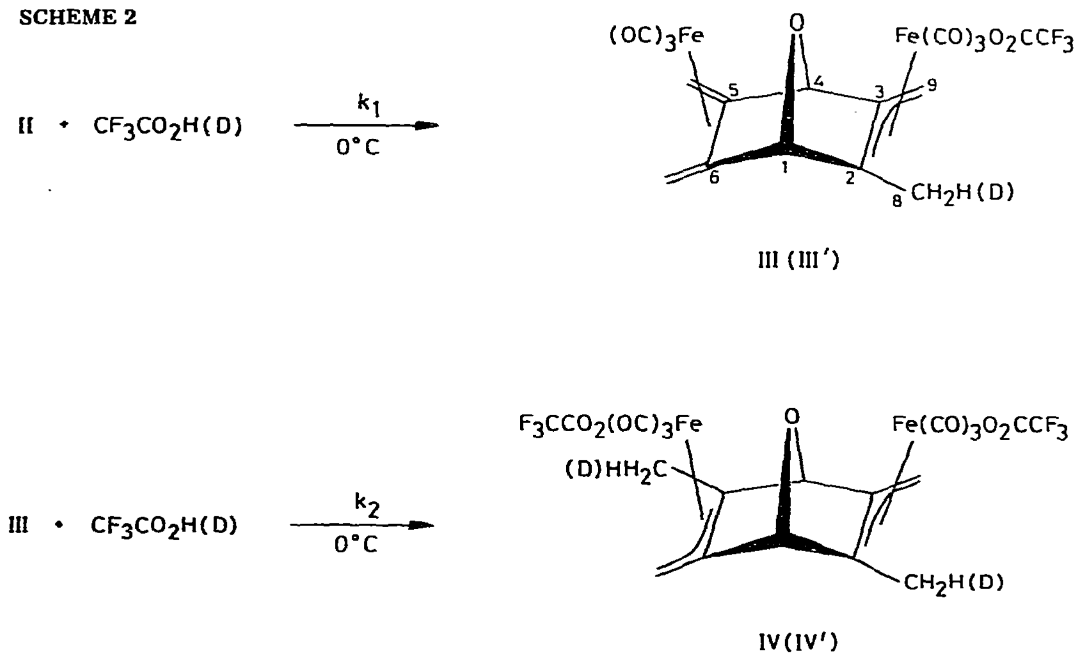
two $Fe(CO)_3$ groups are in the *exo* position with respect to the roof-shaped ligand, as found for complex II in solution. The arrangements of ligands about the iron atoms are tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints of the exocyclic C—C bonds of one *s-cis*-butadiene system, and define the basal plane (Table 5). The diene is perpendicular to the basal plane and the apical Fe—CO bond makes an angle of 8(1)° with the normal to the basal plane. However, the terminal hydrogen atoms are out of the diene plane. The mean dihedral angles between the planes C—C—H(*E* or *Z*) and the diene plane are 15° (towards the Fe atom) and 38° (away from Fe), and are in agreement with the deviations reported for similar structures [11].

The distance between the terminal carbons of the coordinated dienes (2.835(8) Å) of II is somewhat larger than that measured in the corresponding bis(iron tricarbonyl) complex of 5,6,7,8-tetrakis(methylene)-bicyclo[2.2.2]loct-2-ene $(C_{12}H_{12})Fe(CO)_6$ (2.736(8) Å [12]). A similar trend in the 1,4-distance between the terminal carbons of the free diene is also expected for exocyclic dienes grafted onto bicyclic skeletons [13]. The coordination polyhedrons of Fe(1) and Fe(2) are identical, and similar to that already discussed for $(C_{10}H_{10}O)Fe(CO)_3$ (*endo*) [2].

Regioselective double addition of a protic acid

In the presence of strong protic acids, the free ligand I leads to fast polymerisation. In an excess of $CF_3CO_2D/CHCl_3$, complex II added sequentially two equivalents of acid without the formation of polymers. The reaction could be followed by ^1H NMR in a sealed tube under pseudo first order conditions ($[CF_3CO_2D]/[II] = 20$; $CDCl_3$; 0°C). Successive integrations of the spectra indicated a gradual decrease in intensity of a set of signals attributable to II, an increase followed by a decrease of a second set of resonances which chemical shifts and coupling constants were identical to those of complex III' (Scheme 2)

SCHEME 2



prepared independently (Experimental), and a gradual increase of a third set of signals attributable to complex IV'. Thus, the addition of CF_3CO_2D proceeds in two successive stoichiometric steps (Scheme 2). Their kinetics were simulated with the program ITERAT [14] (Fig. 2) giving the two pseudo first order rate constants $k_1[D^+] = (5.5 \pm 0.1) \times 10^{-4}\ s^{-1}$ and $k_2[D^+] = (4.3 \pm 0.1) \times 10^{-5}\ s^{-1}$

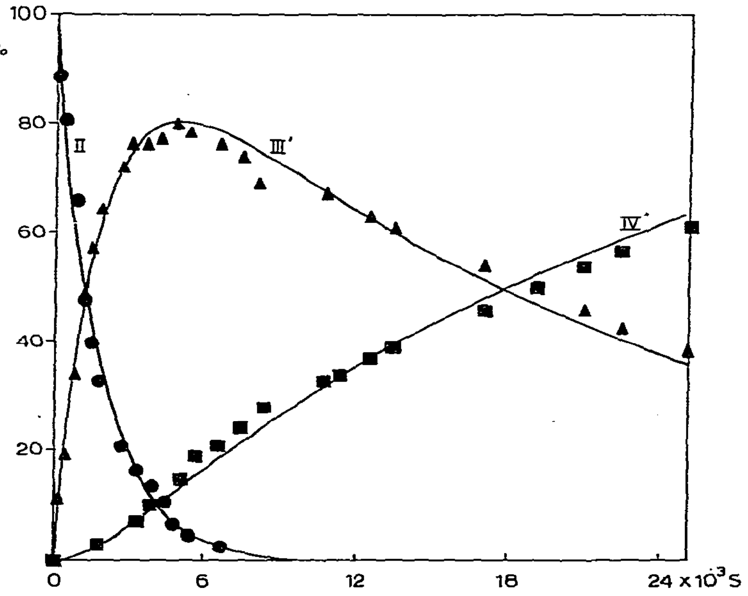
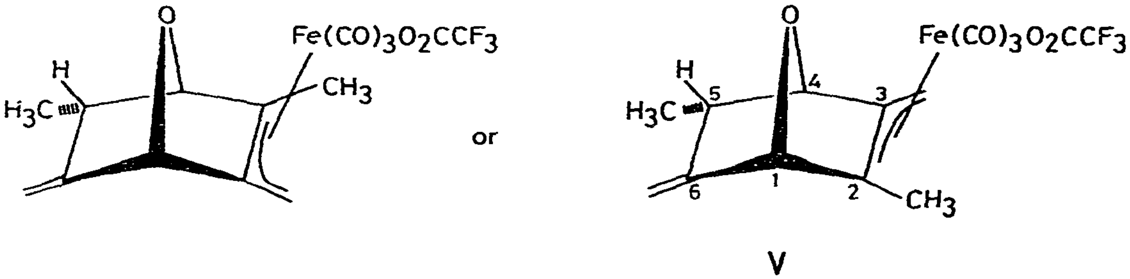


Fig. 2. Progress of the reaction II + CF_3CO_2D (molar ratio 1/20) in $CDCl_3$ at 0°C.

at 0° C (Experimental). The final deuterium content of complex IV′ was 93 ± 5%, and deuterium incorporation occurred only at one terminal carbon atom of each *s-cis*-butadiene system.

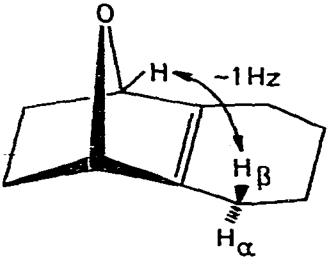
Complexes III and IV are stable in the solid state. Upon standing for two weeks at 0° C in dry diethyl ether, IV underwent a slow decomposition to give the complex V, formally a product of dismutation of IV (40%).

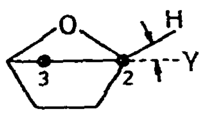


V

The ^1H and ^{13}C NMR spectral data for I and II have been reported elsewhere [2]. Those of complexes III—V are reported in Table 6 and the IR data and microanalyses in the Experimental part.

The ^1H NMR spectrum of III presents 9 resonances indicative of a C_1 symmetry. The two pairs of doublets at ca. 2.5 and 1 ppm are due to the magnetically non-equivalent methylenic protons H(10, 11*E*) and H(10, 11*Z*) of an (exocyclic diene-1,3)Fe(CO)$_3$ group as deduced from a comparison of the $^1J(E, Z)$ coupling constants and $\Delta\delta = \delta$(ligand I) — δ(complex) with the corresponding values for complex II and for the tricarbonyliron complexes of 2,3-bis(methylene)bicyclo [2.2.2]octane [15] and 2,3,5,6-tetrakis(methylene)-bicyclo[2.2.2]octane [12]. The magnitude of the ^5J(H(1), H(10E)) (or ^4J(H(4), H(10E)) $\simeq$ 1 Hz) between the bridgehead and methylenic (*E*) protons may be used as a probe of the *exo* or *endo* position of the iron atom with respect to the roof-shaped ligand. This coupling is observed for II, III and (C$_{10}$H$_{10}$O)Fe(CO)$_3$(*exo*) [2], but not for the *endo* isomer (C$_{10}$H$_{10}$O)Fe(CO)$_3$ [2]. It is comparable to the ^5J coupling constant between the β-allylic and the bridgehead protons observed for cyclohexenes annelated to 7-oxanorbornenes [16]. Such long range coupling was not observed in the ^1H NMR spectra of bicyclo[2.2.2]octenes [12,14], probably because of a smaller dihedral angle between the bridgehead hydrogens and the C(2, 3) bond in the latter systems (ii) than in the former (i). The comparison of the crystal structures of II (vide supra) and (C$_{10}$H$_{10}$O)Fe(CO)$_3$ (*endo*) [2] shows that the dihedral angle between planes H(10E)—C(10)—C(5) and C(5)—C(4)—H(4) is close to 0° for the *exo*





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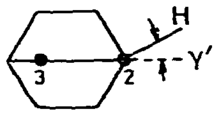


ii

TABLE 6

^{1}H AND ^{13}C NMR SPECTRAL DATA FOR THE PRODUCTS OF PROTON ADDITION [a]

III and III′ [b]			IV and IV′			V	
H(1)		5.66(s, 1) [c]	H(1,4)		5.41(s, 2) [c]	H(1)	5.24(bs, 1) [c]
H(4)		5.34(s, 1)				H(4)	4.53(d, 1)
H(8)	III′:	1.45(bt, 2) [d]	H(8,10)	IV′:	1.51(bs, 4) [d]	H(5)	2.87(m, 1)
	III:	1.44(s, 3)		IV:	1.50(s, 6)	H(8)	1.22(s, 3)
H(9*E*)		5.41(d, 1) [e]	H(9,11*E*)		5.50(d, 2) [e]	H(9*E*)	5.44(m, 1)
H(9*Z*)		3.20(d, 1)	H(9,11*Z*)		3.34(d, 2)	H(9*Z*)	2.88(m, 1)
H(10,11*E*)		2.69, 2.47(d, 1) [f]				H(10)	1.29(d, 3)
H(10,11*Z*)		1.15, 1.04(d, 1)				H(11*E*)	5.09(d, 1)
C(1,4)		86.2, 84.5(d) [g]	C(1,4)		89.9(d) [h]	H(11*Z*)	5.23(m, 1)
C(2)		102.7(s)	C(2,5)		97.3(s)	*J*(H(4), H(5))	4.4
C(3)		124.0(s)	C(3,6)		123.4(s)	*J*(H(5), H(10))	7.0
C(5,6)		113.5, 109.3(s)				*J*(H(9*E*,*Z*))	2.7
C(8)	III′:	15.2(tt) [i]	C(8,10)	IV′:	15.2(tt) [i]	*J*(H(11*E*,*Z*))	0.9
	III:	15.5(q)		IV:	15.4(q)	*J*(H(11*E*), H(5))	2.2
C(9)		63.6(t)	C(9,11)		63.6(t)		
C(10, 11)		35.8, 35.7(t)					
CF_3		115.3(q) [j]	CF_3		115.3(q) [j]		
COO		161.1(q) [k]	COO		161.2(q) [k]		
CO		205.7, 205.2, 204.6(s) 211.3(s) [l]	CO		205.6, 205.4, 204.1(s)		

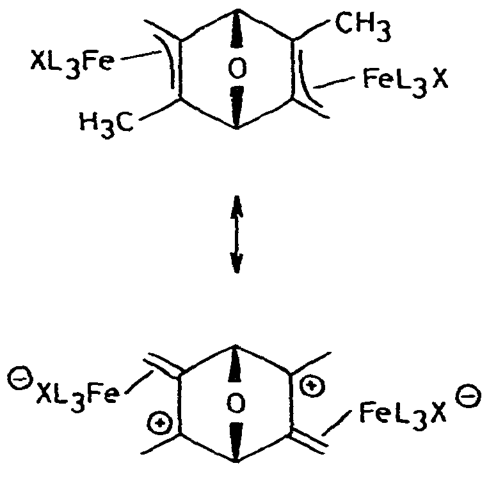
[a] ^{1}H FT NMR (360 MHz) in acetone-d_6 at −20°C for III and III′, at room temperature for IV, IV′ and V′. ^{13}C FT NMR (90.55 MHz) in acetone-d_6 at −20°C. Spectral data for II: see ref. 2. [b] Numbering scheme in Scheme 2. [c] From left to right: $\delta \pm 0.02$ ppm relative to TMS, in parentheses: multiplicity and relative integration. [d] $J(\mathrm{H,D}) < 1$ Hz. [e] $J(E,Z)$ 2.0 ± 0.3 Hz. [f] $J(E,Z)$ 2.8 ± 0.3 Hz. [g] $^1J(\mathrm{C,H}) \pm 1$ Hz: 171, 131, 165 and 164 Hz for C(1), C(8), C(9) and C(10), respectively. [h] $^1J(\mathrm{C,H}) \pm 1$ Hz: 174, 130 and 165 Hz for C(1), C(8) and C(9), respectively. [i] $^1J(\mathrm{C,D})$ 19 ± 2 Hz. [j] $^1J(\mathrm{C,F})$ 290 ± 1 Hz. [k] $^2J(\mathrm{C,F})$ 37 ± 1 Hz. [l] Intramolecular CO exchange of the (diene)Fe(CO)$_3$ group blocked at −53°C; δ 215.3, 209.9 and 209.2 ppm.

isomer and close to 70° for the *endo* isomer. As this difference is in accordance with the corresponding ^5J (or ^4J's), we conclude that the diene iron atom of III is still in the *exo* position. No epimerisation has thus occurred and the addition of acid took place only at one of the two (diene)Fe(CO)$_3$ groups of II. Complete transfer of D^+ (or H^+) occurred to one terminal carbon atom of the diene as shown by the relative intensities of the H(8) signals in the ^{1}H NMR spectra of III′ and III, and by a multiplet typical for a CH_2D group (^1J(C, D) 19 Hz, ^1J(C, H) 131 Hz) in the ^{13}C NMR spectrum of III′ (Table 6). No high field hydridic resonance was found at low temperature which would be indicative of a Fe . . . H . . . C bridge as observed by Ittel et al. [17] for Fe(η^3-C_8H_{13})[P(OMe)$_3$]$_3^+$ (resulting from the addition of HBF_4 to the η^4-cyclooctadiene complex). This is probably due to the presence of the conjugate base $CF_3CO_2^-$ which releaves the electronic and coordinative unsaturation of the allyl-Fe(CO)$_3$ cation. Indeed, complex IV, and most probably III, are feebly dissociated species, since the measured equivalent conductance of IV in nitromethane at 24°C was 6.3 Ω^{-1} cm^2 mol^{-1} (a characteristic Λ for a 1 : 1 salt in the same solvent is ca. 10^2 Ω^{-1} cm^2 mol^{-1} [18]).

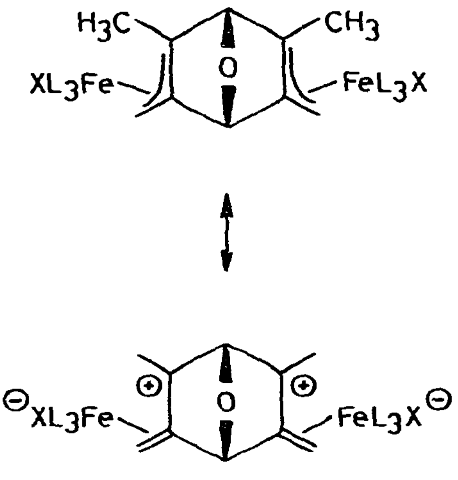
Compound IV must be a bis(allyl) complex formed by addition of CF_3CO_2H to the (diene)Fe(CO)$_3$ system of III, since only four resonances are present in its ^{1}H NMR spectrum (360 MHz). The magnetic equivalence of the bridgehead protons H(1, 4) indicates that the allyl groups are symmetrical with respect to rotation around the C_2 axis passing through O(7). The relative intensities of the H(8, 10) signals of IV′ (dideuterated) and IV (undeuterated complex), and the observed ^1J(C, D) coupling constant, indicate the presence of two —CH_2D groups. Thus, the addition of the D^+ ion took place on the terminal diene carbon atom in a *trans* position with respect to the —CH_2D group of III′.

The ^{1}H NMR spectrum (360 MHz) of the product V presents 9 signals indicative of a C_1 symmetry (Table 6). The assignments were deduced from selective irradiation experiments. The doublet at 4.03 ppm must be due to H(4), the only bridgehead proton which may couple with H(5). The observed ^3J(H(4), H(5)) of 4.4 Hz is typical for an *exo* configuration of H(5) as reported for derivatives of norbornene [19] and oxanorbornene [20]. By irradiating H(4) (δ 4.53 ppm), the multiplet attributed to H(5) became a quadruplet, thus confirming the tertiary methyl group at C(5). The long-range coupling constant observed for the η^4-*exo*-Fe(CO)$_3$ complexes II and III between the H(*E*) of the coordinated diene and the bridgehead hydrogens H(1, 4) is not observable in the corresponding η^3-allyl-Fe(CO)$_3$ trifluoroacetates III, IV and V. Thus, the two proposed geometries for complex V are undistinguishable.

The slower protic acid addition to III than that to II ($k_2/k_1 \simeq 0.1$) can be attributed to the differential field effect of the homoconjugated diene-Fe(CO)$_3$ and methylallyl-Fe(CO)$_3$ trifluoroacetate on the basicity of an exocyclic diene-Fe(CO)$_3$ function grafted onto the 7-oxanorbornane skeleton. The absence of further deuterium uptake of the monodeuterated adduct III′ and bis-deuterated bis-adduct IV′ upon standing in an excess of CF_3CO_2D at 0°C demonstrates that the high regioselectivity of the addition III + $CF_3CO_2H \rightarrow$ IV is a kinetic effect rather than a thermodynamic effect, although it parallels the expected stability difference between the dicationic species j and jj. In the *trans* bis-adduct j, the average distance between the two positive charges is expected to



j



jj

be longer than in the case of the *cis* bis-adduct jj, thus making j more stable than jj.

A similar reactivity trend (k_1/k_2) and regioselectivity can be expected for reactions of II with electrophiles other than CF_3CO_2H. Work is under way to scrutinize this question and to develop the regiospecific double substitution of the tetraene I.

Experimental

All reactions were carried out under argon and the solvents were dried and degassed by standard methods [21]. IR spectra in Nujol were measured with a Perkin-Elmer 577 spectrophotometer; ^1H (360 MHz) and ^{13}C (90.55 MHz) NMR spectra with a Bruker WH 360 spectrometer (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 [16,2].

Kinetic measurements

A solution of CF_3CO_2D and II (molar ratio = 20) in $CDCl_3$ was sealed in an NMR tube under argon and its ^1H NMR spectrum measured at 0°C with a Bruker WP 80 spectrometer. Successive integrations of the spectra indicated a gradual decrease in intensity of the three resonances of III (δ(H(1, 4)) 5.15, δ(H(8—11*E*)) 2.33 and δ(H(8—11*Z*)) 0.76 ppm) which disappeared after ca. 160 min. A second set of 9 resonances increased in intensity, passing through a maximum after ca. 80 min, and then decreased while a third set of 4 resonances was continually increasing in intensity. The set of 9 resonances could be related to those of an authentic sample of III′. Isolation of the final product after 12 h of reaction by extraction with CH_2Cl_2/aqueous $(NH_4)_2SO_4$ gave a yellow powder which spectral data were identical to those of an authentic sample of IV′. The observed relative concentrations of II, III′ and IV′ (% vs. *t*) are given in Fig. 2. As the addition of acid clearly corresponds to two succes first order reactions, the following equations were used in the fitting procedure:

$$[\mathrm{II}] = [\mathrm{II}]_0\, e^{-k'_1 t}\,; \qquad [\mathrm{III}'] = \frac{[\mathrm{II}]_0 k'_1}{k'_2 - k'_1}\,(e^{-k'_1 t} - e^{-k'_2 t})$$

$$[\mathrm{IV}'] = [\mathrm{II}]_0 \left\{1 + \frac{1}{k'_1 - k'_2}\,(k'_2\, e^{-k'_1 t} - k'_1\, e^{-k'_2 t})\right\}$$

where $[II]_0$ = initial relative concentrations of II (100%) and $k'_i = k_i[\mathrm{D}^+]$. The rate constants k'_1 and k'_2 were then calculated by ITERAT, a general program of least-squares non linear regression for NORSK-10/S (plain curves in Fig. 2)

Preparation of complexes

a) An excess of anhydrous CF_3CO_2H was added dropwise to a solution of I (0.3 g; 0.7 mmol) in dichloromethane (80 ml). After stirring for 90 min at room temperature, saturated aqueous $(NH_4)_2SO_4$ (50 ml) was added. The organic extract was washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. The residue was taken up in diethyl ether, from which con plex IV precipitated out as pale yellow powder (0.284 g, yield 62%).

IV: m.p. 98—100°C. Analysis. Found: C, 36.65; H, 1.72; F, 17.17. $C_{20}H_{12}O_{11}F_6Fe_2$ calcd.: C, 36.73; H, 1.85; F, 17.43%. IR: ν(CO) 2117, 2065, 2040 cm^{-1}; ν(C=O) 1692 cm^{-1}.

The same reaction with CF_3CO_2D, but replacing $(NH_4)_2SO_4/H_2O$ by Na_2CO_3/D_2O, gave IV′ (70%; same m.p. and IR spectrum as IV, NMR data in Table 6).

The monoallyl complex III′ could be isolated only by adding D_2O to CF_3CO_2D which seems to slow down the reaction. Thus, one ml CF_3CO_2D/10 vol.% D_2O was added to a solution of II (0.3 g; 0.7 mmol) in dichloromethane (80 ml). After stirring for 5 h at room temperature, a solution of Na_2CO_3 in D_2O (20 ml) was added, and the organic extract washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. The residue was taken up in ether, from which complex III′ separated as a yellow powder (0.15 g, yield 40%).

III′: m.p. 120—122°C (dec). Analysis. Found: C, 39.75; H, 2.21. $C_{18}H_{10}DO_9F_3Fe_2$ calcd.: C, 39.97; H, 2.05%. IR: ν(CO) 2072, 2063, 2040, 1988, 1977 cm^{-1}; ν(C=O) 1683 cm^{-1}.

The same reaction with CF_3CO_2H gave III (60%; same m.p. and IR spectrum as III′, NMR data in Table 6).

b) A solution of IV in diethyl ether was left at 0°C for one week under argon in the dark. Filtration and cooling at —78°C gave yellow crystals of V (yield 20%).

V: m.p. 93—95°C (dec). Analysis. Found: C, 45.10; H, 3.18. $C_{15}H_{13}O_6F_3Fe$ calcd.: C, 44.81; H, 3.26%. IR: ν(CO) 2098, 2055, 2025 cm^{-1}; ν(C=O) 1687 cm^{-1}.

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