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STEREOSPECIFIC FUNCTIONALISATIONS OF IRON CARBONYL COMPLEXES OF 5,6,7,8-TETRAKIS(METHYLENE)BICYCLO[2.2.2]OCT-2-ENE. CRYSTAL AND MOLECULAR STRUCTURE OF $(C_{12}H_{12})Fe_2(CO)_6$

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Summary

When the reaction between an excess of $Fe_2(CO)_9$ and the pentaene 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (I) is carried out in hexane/methanol the *endo,exo*-bis(tetrahaptotricarbonyliron) isomer $(C_{12}H_{12})Fe_2(CO)_6$ (IIa) is the major product. The structure of this complex has been determined by X-ray diffraction. The asymmetric positions of the two $Fe(CO)_3$ groups with respect to the roof-shaped organic skeleton was used to induce either stereospecific functionalisation of the uncoordinated endocyclic C—C double bond or stereo- and regiospecific functionalisation of one of the two coordinated *s-cis*-butadiene groups of the pentaene. Thus, hydroboration/oxidation of IIa gave the *endo,exo*-bis(tetrahaptotricarbonyliron) isomer of 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]octane-2-ol (IV). *cis* deuteration of the exocyclic double bond was achieved by treating IIa with D_2/PtO_2 in n-hexane.

Protonation of IIa by $HCl/AlCl_3/CH_2Cl_2$ to give the η^4-diene : η^2-ene : η^3-dienyl cationic complex Va, followed by quenching of Va with $NaHCO_3/CH_3OH$, resulted in a 1,4-addition of methanol to one coordinated *s-cis*-butadiene system. In contrast, quenching with $NaOCH_3/CH_3OH$ resulted in the corresponding 1,2-addition of methanol. This gave the η^4-1,3-diene : η^4-1,4-diene complex VIIIa in which, suprisingly, one $Fe(CO)_3$ group is coordinated to two C—C double bonds in *gauche* positions with respect to each other.

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Introduction

We reported recently [1,2] 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. One of the bimetallic complexes, viz the *endo,exo*-bis(tetrahaptotricarbonyliron) isomer $(C_{12}H_{12})Fe_2(CO)_6$ (IIa, Scheme 1), should be an useful synthon. It does not epimerise in solution to the *diexo* isomer, and so it would be expected that the asymmetric positions of the two $Fe(CO)_3$ groups with respect to the roof-shaped organic skeleton could be used either to achieve a stereospecific attack of the uncoordinated endocyclic double bond by electrophiles or to functionalise regioselectively one of the two coordinated *s-cis*-butadiene systems of the pentaene, and, indeed, stereospecific monoacetylation of I has been achieved in this way [3]. We report here some results on the hydroboration, deuteration and protonation of IIa, as well as an X-ray crystal structure determination of $(C_{12}H_{12})Fe_2(CO)_6$.

Results and discussion

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

X-Ray measurements were carried out with a Syntex $P2_1$ automatic diffractometer. The methods used and results obtained are shown in Table 1.

The crystal form was accurately measured as before [5] and used to 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

TABLE 1

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

Formula	$(C_{12}H_{12})Fe_2(CO)_6$ $C_{18}H_{12}O_6Fe_2$	Radiation	Mo-K_α, Nb filtered $\lambda = 0.71069$ Å
Mol. weight	435.98	μ(cm^{-1})	17.06
Dimensions(mm)	0.17 X 0.18 X 0.23	Scan method	2θ—θ
Crystal system	Orthorhombic	Background from	Scan profile interpretation [4]
a(Å)	12.472(2)	$(\sin\theta/\lambda)$max	0.54
b(Å)	12.580(2)	Data collected	$k, k, l > 0$
c(Å)	22.666(4)	No. of unique reflections	2411
V(Å^3)	3556(2)	No. of reflections $< 3\sigma$	1095
Z	8	No. of observations/No of variables	8.3
d_{calcd}(g/cm^3)	1.63		
d_{obsd}(g/cm^3)	1.63(1)	Structure solutions	Patterson and Fourier
F_{000}	1760	Refinement	Block diagonal least-squares
Space grpup	*Pbca*	Function minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Systematic absences	$0\,k\,l : k = 2n + 1$	w	$1/\sigma^2$
	$h\,0\,l : l = 2n + 1$	R	0.046
	$h\,k\,0 : h = 2n + 1$	R_w	0.031
		Goodness of fit	1.62

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}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.40859(7)	0.36338(6)	0.24438(4)	0.0486(5)	0.0376(4)	0.0381(4)	0.0054(6)	−0.0043(6)	−0.0030(5)
Fe(2)	0.49825(9)	0.23178(7)	0.45864(4)	0.0697(6)	0.0539(5)	0.0397(4)	−0.0038(7)	0.0028(7)	0.0024(5)
C(1)	0.5707(6)	0.3972(5)	0.3543(3)	0.031(5)	0.048(5)	0.048(4)	−0.010(4)	0.004(4)	0.001(3)
C(2)	0.5289(7)	0.5110(6)	0.3494(3)	0.065(7)	0.045(5)	0.052(5)	−0.020(5)	−0.008(5)	−0.003(4)
C(3)	0.4281(7)	0.5225(6)	0.3646(3)	0.073(7)	0.040(5)	0.051(4)	0.003(6)	−0.003(5)	−0.007(4)
C(4)	0.3733(6)	0.4205(5)	0.3832(3)	0.042(5)	0.047(4)	0.041(4)	0.004(4)	0.009(4)	−0.011(3)
C(5)	0.4426(6)	0.3833(5)	0.4351(3)	0.056(6)	0.036(6)	0.035(4)	−0.002(4)	−0.006(4)	−0.009(3)
C(6)	0.5498(6)	0.3698(6)	0.4198(3)	0.054(5)	0.051(4)	0.038(4)	−0.008(4)	−0.010(4)	−0.002(4)
C(7)	0.4955(5)	0.3258(4)	0.3190(2)	0.034(4)	0.032(4)	0.034(3)	−0.001(4)	0.005(4)	−0.001(3)
C(8)	0.3886(5)	0.3385(4)	0.3347(2)	0.036(4)	0.026(4)	0.037(3)	0.011(4)	0.002(3)	−0.003(3)
C(9)	0.4115(8)	0.3593(7)	0.4942(3)	0.082(7)	0.071(5)	0.046(5)	−0.015(6)	−0.001(6)	−0.016(5)
C(10)	0.6238(7)	0.3412(7)	0.4639(3)	0.066(6)	0.076(6)	0.049(5)	0.003(5)	−0.007(5)	0.001(5)
C(11)	0.5207(6)	0.2516(6)	0.2743(3)	0.045(6)	0.043(4)	0.047(4)	0.005(5)	0.004(4)	−0.002(3)
C(12)	0.3106(7)	0.2799(6)	0.3046(3)	0.038(5)	0.041(5)	0.062(5)	−0.001(5)	−0.004(4)	−0.010(4)
C(13)	0.3224(5)	0.4757(5)	0.2410(3)	0.046(4)	0.053(4)	0.036(4)	−0.005(4)	−0.000(4)	−0.001(4)
C(14)	0.3623(5)	0.2909(5)	0.1832(3)	0.066(5)	0.040(4)	0.053(4)	0.003(4)	−0.012(4)	0.000(3)
C(15)	0.5121(6)	0.4355(5)	0.2109(3)	0.066(5)	0.048(4)	0.034(4)	0.013(5)	−0.008(4)	0.001(3)
C(16)	0.5286(7)	0.1809(6)	0.5291(3)	0.121(8)	0.086(6)	0.067(5)	0.006(6)	0.018(6)	0.004(5)
C(17)	0.3805(7)	0.1628(6)	0.4395(3)	0.079(6)	0.057(6)	0.074(5)	−0.010(5)	0.021(5)	−0.006(4)
C(18)	0.5758(6)	0.1450(6)	0.4155(3)	0.063(6)	0.054(5)	0.054(4)	−0.012(5)	0.003(4)	0.001(4)
O(1)	0.2682(4)	0.5497(3)	0.2372(2)	0.067(4)	0.053(3)	0.078(3)	0.021(3)	0.007(3)	0.004(3)
O(2)	0.3292(4)	0.2454(3)	0.1425(2)	0.096(4)	0.066(3)	0.069(3)	0.006(4)	−0.027(3)	−0.023(3)
O(3)	0.5803(4)	0.4819(4)	0.1875(2)	0.071(4)	0.069(3)	0.061(3)	−0.005(3)	0.007(3)	0.005(3)
O(4)	0.5516(6)	0.1508(5)	0.5760(2)	0.215(8)	0.176(6)	0.061(3)	0.044(6)	0.012(5)	0.050(4)
O(5)	0.3034(5)	0.1160(4)	0.4279(2)	0.091(5)	0.094(5)	0.116(4)	−0.033(4)	0.030(4)	−0.021(4)
O(6)	0.6278(4)	0.0851(4)	0.3893(2)	0.088(5)	0.081(4)	0.095(4)	0.008(4)	0.017(3)	−0.013(3)
H(1)	0.646(4)	0.389(4)	0.341(2)	0.03(2)					
H(2)	0.578(4)	0.557(4)	0.332(2)	0.06(2)					
H(3)	0.386(4)	0.587(4)	0.357(2)	0.06(2)					
H(4)	0.300(4)	0.428(4)	0.393(2)	0.03(2)					
H(10*E*)	0.693(4)	0.321(4)	0.451(2)	0.03(2)					
H(10*Z*)	0.611(4)	0.370(4)	0.504(2)	0.05(2)					
H(11*E*)	0.590(4)	0.252(4)	0.262(2)	0.01(2)					
H(11*Z*)	0.481(4)	0.181(4)	0.274(2)	0.05(2)					
H(12*E*)	0.242(4)	0.306(4)	0.308(2)	0.02(2)					
H(12*Z*)	0.318(4)	0.202(4)	0.293(2)	0.05(2)					
H(9*E*)	0.331(4)	0.351(4)	0.502(2)	0.06(2)					
H(9*Z*)	0.448(4)	0.389(4)	0.521(2)	0.04(2)					

TABLE 3

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

Fe(1)—C(13)	1.777(6)	Fe(2)—C(16)	1.762(7)
Fe(1)—C(14)	1.758(6)	Fe(2)—C(17)	1.760(8)
Fe(1)—C(15)	1.751(7)	Fe(2)—C(18)	1.756(7)
Fe(1)—C(7)	2.085(5)	Fe(2)—C(5)	2.098(6)
Fe(1)—C(8)	2.063(6)	Fe(2)—C(6)	2.050(7)
Fe(1)—C(11)	2.112(8)	Fe(2)—C(9)	2.096(9)
Fe(1)—C(12)	2.095(7)	Fe(2)—C(10)	2.089(8)
C(13)—O(1)	1.154(7)	C(16)—O(4)	1.164(9)
C(14)—O(2)	1.160(7)	C(17)—O(5)	1.160(9)
C(15)—O(3)	1.161(8)	C(18)—O(6)	1.158(9)
C(1)—C(2)	1.53(1)	C(4)—C(3)	1.51(1)
C(1)—C(6)	1.546(8)	C(4)—C(5)	1.534(9)
C(1)—C(8)	1.525(9)	C(4)—C(7)	1.519(8)
C(2)—C(3)	1.31(1)		
C(5)—C(6)	1.39(1)	C(7)—C(8)	1.389(9)
C(5)—C(9)	1.426(9)	C(7)—C(11)	1.398(9)
C(6)—C(10)	1.41(1)	C(8)—C(12)	1.413(9)
C(1) —H(1)	0.98(5)	C(4) —H(4)	0.94(5)
C(2) —H(2)	0.93(5)	C(3) —H(3)	0.97(5)
C(9) —H(9*E*)	1.02(5)	C(11)—H(11*E*)	0.92(5)
C(9) —H(9*Z*)	0.84(5)	C(11)—H(11*Z*)	1.02(5)
C(10)—H(10*E*)	0.94(5)	C(12)—H(12*E*)	0.91(5)
C(10)—H(10*Z*)	0.99(5)	C(12)—H(12*Z*)	1.01(5)

was solved by Patterson and Fourier methods. Hydrogen atoms were located after refinement to $R = 0.062$, and refinement continued to $R = 0.046$. The final positional and thermal parameters are listed in Table 2 *. One CO group (C(16)—O(4)) has high thermal motion. Treating this as evidence of disorder, the two atoms were split along the longest vibration axis and refined as half-atoms. This did not improve the model, and so the high thermal parameters were accepted as real. Calculated bond lengths and angles are listed 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, prepared by the program ORTEP [10] is given in Figure 1, where the numbering scheme is indicated. For the ligand, the numbering scheme is identical with that used for nomenclatural purposes.

The structure is composed of discrete $(C_{12}H_{12})Fe_2(CO)_6$ molecules. All intermolecular contacts are equal to or greater than the sum of Van der Waals radii. The two $Fe(CO)_3$ groups are in *trans* positions with respect to the roof-shaped ligand. Thus, the geometry is the same in the solid state as in solution and confirms the assignments of the NMR spectra made previously [1]. There is essentially mirror symmetry for the whole molecule, with the mirror plane I (Table 5) passing through the two Fe atoms and two CO groups. The carbon skeleton is undistorted, as shown by the coplanarity of C(1—4) (plane II) and of the carbon atoms of each *s-cis*-butadiene system (planes III—VI). The arrangement of ligands about each Fe atom is tetragonal pyramidal. Four coordination sites

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

TABLE 4

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

C(7)—Fe(1)—C(11)	38.9(3)	C(5)—Fe(2)—C(9)	39.8(3)
C(7)—Fe(1)—C(8)	39.1(2)	C(5)—Fe(2)—C(6)	39.2(3)
C(8)—Fe(1)—C(12)	39.7(2)	C(6)—Fe(2)—C(10)	39.8(3)
C(11)—Fe(1)—C(12)	80.9(3)	C(9)—Fe(2)—C(10)	81.9(3)
C(13)—Fe(1)—C(14)	100.3(3)	C(16)—Fe(2)—C(17)	102.9(4)
C(13)—Fe(1)—C(15)	90.8(3)	C(17)—Fe(2)—C(18)	90.9(3)
C(14)—Fe(1)—C(15)	99.7(3)	C(16)—Fe(2)—C(18)	99.2(3)
Fe(1)—C(13)—O(1)	177.9(5)	Fe(2)—C(16)—O(4)	177.2(7)
Fe(1)—C(14)—O(2)	177.8(6)	Fe(2)—C(17)—O(5)	178.6(6)
Fe(1)—C(15)—O(3)	178.3(5)	Fe(2)—C(18)—O(6)	176.9(6)
C(2)—C(1)—C(6)	102.8(5)	C(3)—C(4)—C(5)	102.6(6)
C(2)—C(1)—C(8)	107.7(6)	C(3)—C(4)—C(7)	108.5(6)
C(6)—C(1)—C(8)	105.6(5)	C(5)—C(4)—C(7)	106.1(5)
C(1)—C(2)—C(3)	114.3(7)	C(2)—C(3)—C(4)	114.3(7)
C(1)—C(6)—C(5)	112.0(6)	C(4)—C(5)—C(6)	112.7(5)
C(1)—C(6)—C(10)	129.0(7)	C(4)—C(5)—C(9)	129.2(7)
C(5)—C(6)—C(10)	118.9(6)	C(6)—C(5)—C(9)	118.0(7)
C(4)—C(7)—C(8)	112.8(5)	C(1)—C(8)—C(7)	112.5(5)
C(4)—C(7)—C(11)	129.0(6)	C(1)—C(8)—C(12)	128.6(6)
C(8)—C(7)—C(11)	118.8(5)	C(7)—C(8)—C(12)	118.2(6)
H(1)—C(1)—C(2)	114(3)	H(4)—C(4)—C(3)	115(3)
H(1)—C(1)—C(6)	115(3)	H(4)—C(4)—C(5)	114(3)
H(1)—C(1)—C(7)	111(3)	H(4)—C(4)—C(8)	110(3)
H(2)—C(2)—C(1)	113(3)	H(3)—C(3)—C(4)	120(3)
H(2)—C(2)—C(3)	132(3)	H(3)—C(3)—C(2)	124(3)
C(5)—C(9)—H(9*E*)	117(3)	C(7)—C(11)—H(11*E*)	115(3)
C(5)—C(9)—H(9*Z*)	116(3)	C(7)—C(11)—H(11*Z*)	124(3)
H(9*E*)—C(9)—H(9*Z*)	116(4)	H(11*E*)—C(11)—H(11*Z*)	116(4)
C(6)—C(10)—H(10*E*)	117(3)	C(8)—C(12)—H(12*E*)	116(3)
C(6)—C(10)—H(10*Z*)	117(3)	C(8)—C(12)—H(12*Z*)	118(3)
H(10*E*)—C(10)—H(10*Z*)	122(4)	H(12*E*)—C(12)—H(12*Z*)	118(4)

are occupied by 2 CO and the midpoints of the outer C—C bonds of one diene system. In both polyhedra the apex-to-base angles are 100° for the carbonyl groups and 112° for the C—C bond midpoints. The basal angles are 91, 94 and 63°, the small angle being that subtended by the two outer C—C bonds of the diene. The diene is perpendicular to the basal plane and the Fe atom lies 0.5 Å above it. The apical Fe—CO bond makes an angle of 8° with the normal to the basal plane. The three C—C distances of each diene are equal within 2σ and the sum of angles at the "inner" carbon atoms is 360.0(6)°. In contrast, H(*Z*) atoms deviate from the diene plane away from the metal by 40° and H(*E*) atoms deviate towards the metal by 11°. These values are in agreement with the mean deviations found from a statistical comparison of 7 (1,3-diene)$Fe(CO)_3$ structures [11]. The shortest interatomic contact is C(15)···C(2) (3.17 Å).

Stereospecific deuteration

The reaction of the pentaene I with $Fe_2(CO)_9$ in n-hexane gives the two $(C_{12}H_{12})Fe(CO)_3$ isomers (*endo* and *exo*), and the two bimetallic isomers $(C_{12}H_{12})Fe_2(CO)_6$ (IIa: *endo,exo*; IIb: *diexo*) in rather low yields [1]. In con-

TABLE 5

LEAST-SQUARES PLANES OF IIa

Plane	Atoms defining the plane [a]	Equation of mean plane
I	Fe(1), C(14), O(2), Fe(2), C(16), O(4)	$11.754X - 2.222Y - 6.433Z = 2.418$
II	C(1), C(2), C(3), C(4)	$3.412X + 2.130Y + 21.460Z = 10.394$
III	C(1), C(4), C(5), C(6)	$2.261X + 11.967Y + 5.649Z = 8.043$
IV	C(1), C(4), C(8), C(7)	$1.222X - 9.022Y + 15.639Z = 2.655$
V	C(5), C(6), C(9), C(10)	$1.893X + 12.072Y + 5.371Z = 7.781$
VI	C(7), C(8), C(11), C(12)	$1.046X - 3.128Y + 15.480Z = 2.489$
VII	m′, m″, C(17), C(18)	$2.533X - 2.995Y + 21.527Z = 9.953$
VIII	m‴, m⁗, C(13), C(15)	$3.852X + 8.364Y + 15.415Z = 8.902$

Displacement of atoms from mean plane (Å)

Plane I		Plane II		Plane III		Plane IV	
Fe(1)	0.006	C(1)	0.002	C(1)	0.001	C(1)	0.0001
C(14)	0.016	C(2)	−0.003	C(4)	−0.001	C(4)	−0.0001
O(2)	−0.010	C(3)	0.003	C(5)	0.003	C(7)	−0.0002
Fe(2)	−0.026	C(4)	−0.002	C(6)	−0.003	C(8)	0.0002
C(16)	−0.009						
O(4)	0.025						

Plane V		Plane VI		Plane VII		Plane VIII	
C(5)	0.021	C(7)	−0.008	m′	0.019	m‴	0.043
C(6)	−0.021	C(8)	0.008	m″	−0.019	m⁗	−0.043
C(9)	−0.011	C(11)	0.004	C(17)	−0.016	C(13)	0.034
C(10)	0.011	C(12)	−0.004	C(18)	0.016	C(15)	−0.034

Dihedral angle between planes (°)

I—II 87.7; I—III 86.1; I—IV 88.7; I—V 84.6; I—VI 89.2; I—VII 87.9; I—VIII 88.9; II—III 116.5; II—IV 124.0; III—IV 119.5; III—V 1.9; IV—VI 1.0; V—VII 88.4; VI—VIII 89.5.

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[a] m′, m″, m‴, m⁗ are the mid-points of the C(5)—C(9), C(6)—C(10), C(7)—C(11) and C(8)—C(12) bonds, respectively.

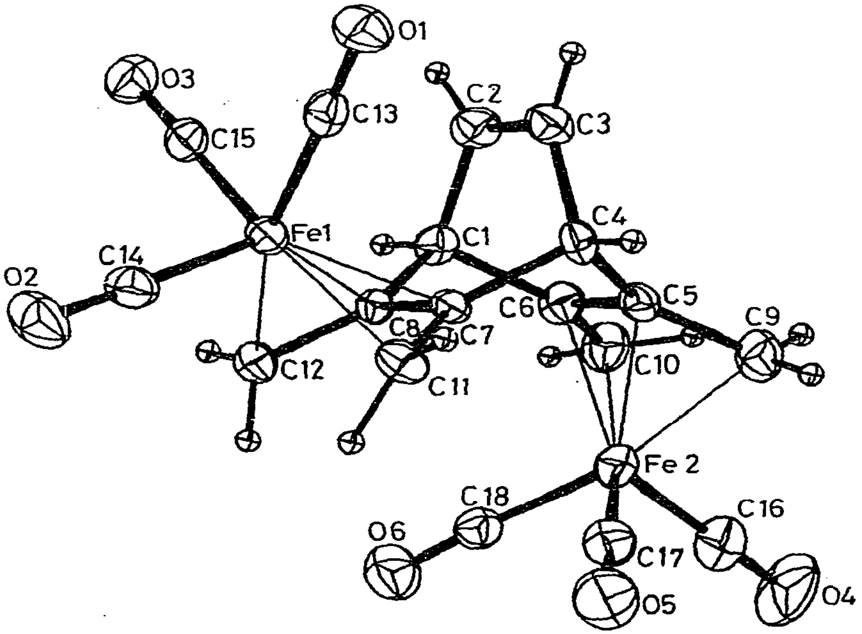
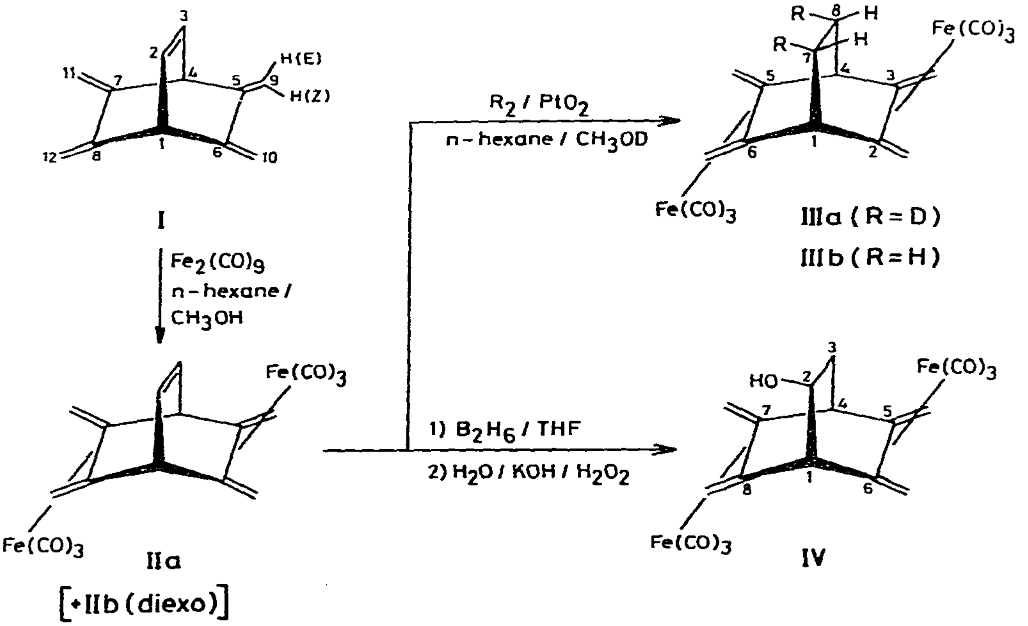


Fig. 1. A perspective view of the molecular structure of $(C_{12}H_{12})Fe_2(CO)_6$ (IIa).

trast, the same reaction in n-hexane/methanol using an excess of $Fe_2(CO)_9$ yields the *endo,exo* isomer IIa as major product (63%, IIb: 2.5%). Such solvent effects on the isomer distribution of (η^4-diene)$Fe(CO)_3$ complexes has not been observed previously, probably because of the unavailability of suitable olefins. However, this effect is known in the case of olefins containing heteroatoms, e.g. Salzer et al. [12] have shown that the reaction of bicyclo[4.2.1]nona-2,4,7-triene-9-one with $Fe_2(CO)_9$ in methanol yields the (2,4-η^4-triene)$Fe(CO)_3$ (*endo*) complex, whereas the *exo* isomer is obtained in benzene. In the present case, the major intermediate formed in methanol is $(C_{12}H_{12})Fe(CO)_3$ (*endo*) (identified by its ^1H NMR spectrum [1]) which then reacts with $Fe_2(CO)_9$ to give IIa, since the *diendo* bimetallic complex cannot be formed for steric reasons. The minor product IIb is formed in a parallel reaction of $(C_{12}H_{12})Fe(CO)_3$ (*exo*) with $Fe_2(CO)_9$.

A clean *cis*-addition of D_2 to the endocyclic double bond of the pentaene occured on stirring a solution of IIa in n-hexane/CD_3OD with PtO_2 as catalyst under 1 atm D_2 (Scheme 1). The product $(C_{12}D_2H_{12})Fe_2(CO)_6$ (*endo, exo*) (IIIa) was obtained in 97% yield with a deuterium incorporation of 95% (measured by mass spectrometry). The hydrogenated product $(C_{12}H_{14})Fe_2(CO)_6$ (*endo, exo*) (IIIb) was obtained on replacing D_2 with H_2 or by the direct reaction of 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane with $Fe_2(CO)_9$ [11]. The comparison of the NMR data of IIIa (Table 6) and IIIb [11] indicates that the deuterium atoms are in *cis* positions since the ^3J(H(7 *syn*),H(7 *anti*)) coupling constant found in IIIb is absent in IIIa. No incorporation of deuterium was observed on reacting the *diexo* isomer IIb and D_2 under the same conditions. Since the $Fe(CO)_3$ groups in the *exo* position seem to prevent a close



SCHEME 1

TABLE 6

^{1}H AND ^{13}C NMR PARAMETERS OF THE PRODUCTS OF DEUTERATION AND HYDROBORATION OF IIa [a]

IIa		IIIa [b]		IV		LIS [d]			LIS
H(1, 4) [c]	4.33(2, dd) [e]	H(1, 4) [c]	3.51(2, bs) [f]	H(1) [c]	3.49 (1, d) [g]	59.2	H(4) [c]	3.43(1, t) [g]	21.6
H(2, 3)	7.03(2, dd)	H(7, 8)	2.19(2, s)	H(2)	4.59(1, m)	100	OH	1.98(1, d)	—
H(9, 10*E*)	2.22(2, d)	H(9, 10*E*)	1.97(2, d)	H(3s)	1.80(1, m)	71.6	H(3a)	2.61(1, m)	37.7
H(9, 10*Z*)	0.52(2, d)	H(9, 10*Z*)	0.38(2, d)	H(9E)	1.87(1, d)	11.5	H(10E)	1.83(1, d)	13.5
H(11, 12*E*)	2.26(2, d)	H(11, 12*E*)	2.20(2, d)	H(9*Z*)	0.38(1, d)	11.3	H(10*Z*)	0.32(1, d)	11.8
H(11, 12*Z*)	0.66(2, d)	H(11, 12*Z*)	0.59(2, d)	H(11*E*)	2.12(1, d)	12.7	H(12*E*)	2.16(1, d)	19.1
				H(11*Z*)	0.63(1, d)	14.8	H(12*Z*)	0.68(1, d)	19.0
C(1, 4) [h]	49.1(d, 141)	C(1, 4) [h]	42.0(d, 143)	C(1) [h]	49.5(d, 143)	46	C(4) [h]	42.8(d, 145)	26
C(2, 3)	140.2(d, 177)	C(2, 3)	113.5(s)	C(2)	71.9(d, 150)	100	C(3)	42.0(t, 135)	43
C(5, 6)	113.3(s)	C(5, 6)	106.8(s)	C(5)	112.0(s)	17	C(6)	107.2(s)	21
C(7, 8)	111.4(s)	C(7, 8)	30.2(d, 130)	C(7)	107.1(s)	26	C(8)	103.6(s)	34
C(9, 10)	38.8(t, 160) [i]	C(9, 10)	36.3(t, 162)	C(9)	37.2(t, 161)	9	C(10)	36.2(t, 160)	10
C(11, 12)	41.0(t, 159)	C(11, 12)	38.4(t, 161)	C(11)	38.2(t, 160)	13	C(12)	40.5(t, 160)	20
CO	211.4(s)	CO	211.0(s)	CO	210.8, 210.6 [j]	6			

[a] The numbering scheme is given in Fig. 1. for IIa, and in Scheme 1 for IIIa and IV. [b] For IIIb, see reference 11. [c] In CD_2Cl_2 at room temperature (80 MHz). From left to right: $\delta \pm 0.02$ ppm relative to TMS, integration, multiplicity. [d] Relative lanthanide induced shift by Eu(dpm)$_3$ for ^{1}H and Yb(dpm)$_3$ for ^{13}C NMR spectra. [e] Coupling constants ±0.2 Hz: ^3J(H(1), H(2)) 4.4; ^4J(H(1), H(3)) 3.0; $|^2J|$(H(9*E*), H(9*Z*)) 2.8; $|^2J|$(H(11*E*), H(11*Z*)) 3.0. [f] $|^2J|$(H9*E*), H(9*Z*)) 2.5; $|^2J|$(H(11*E*), H(11*Z*)) 3.1. [g] ^3J(H(1), H(2)) 3.1; ^4J(H(1), H(3a, 3s)) ~ 0.5; ^3J(H(2), H(3a)) 8.0; ^3J(H(2), H(3s)) 2.2; ^2J(H(3a), H(3s)) 14.0; ^3J(H(3a, 3s), H(4)) 2.8; ^2J(H(2), OH) 5.5; ^4J(H(4), H(2)) ~ 0.5; $|^2J|$(H(9*E*), H(9*Z*)) 3.2; $|^2J|$(H(11*E*), H(11*Z*))2.8. [h] At room temperature in CD_2Cl_2 for IIa, IIIa, in $CDCl_3$ for IV (15.08 MHz). From left to right: $\delta \pm 0.1$ ppm relative to TMS, multiplicity, ^1J(C, H) ± 2 Hz. [i] ^1J(C, H(*Z*)) $\simeq$ ^1J(C, H(*E*)). [j] At −56°C with [Yb]/[IV] = 0.41: δ(CO) 220.1, 218.3, 217.0, 216.4, 215.2, 215.1 ppm.

contact between the endocyclic double bond and the catalyst surface, deuterium addition occurred most probably at the less hindered face of the C(2)—C(3) bond of IIa. A previous example of *cis*-deuteration of the endocyclic double bond of a bicyclic triene has been observed by Steiner et al. [13] in the reaction of (η^4-2,3-bis(methylene)bicyclo[2.2.1]hept-5-ene)tricarbonyliron with D_2/PtO_2.

Stereospecific hydroboration

The two *s-cis*-butadiene systems of IIa are blocked by two $Fe(CO)_3$ groups. The *trans* positions of the latter should direct an electrophile such as B_2H_6 towards the less hindered face of the free endocyclic double bond. IIa reacted cleanly with B_2H_6 in THF and the formed alkylborane was hydrolysed by successive additions of water, KOH, and H_2O_2 at 0°C without extensive decomposition of the complex by the oxidant. Extraction with water/dichloromethane revealed a single product, i.e. the (9,10η^2 : 11,12η^2)$Fe_2(CO)_6$ (*endo*, *exo*) complex of 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]octane-2-ol (IV; 61%) (Scheme 1).

The assignments of the ^1H and ^{13}C NMR signals of IV were based on the shifts induced by $Eu(dpm)_3$ and $Yb(dpm)_3$ respectively *. The LIS's (lanthanide induced shifts) of the CO groups are all equal, and this observation gives unambiguous indication on the position of the OH group. As the paramagnetic center is bonded to the OH group, and is thus in the *exo* position with respect to the roof-shaped ligand, both the OH group and the $Fe(CO)_3$ (*endo*) group must be on the same side of the molecule with respect to the C(1)—C(7)—C(8)—C(4) bridge. Functionalisation has thus occurred on the less hindered face of the endocyclic double bond, as expected. The sequences of decreasing relative LIS's of the 8 diene protons are $H(12Z) > H(11Z)$; $H(12E) > H(11E)$; $H(10E) > H(9E)$ and $H(10Z) > H(9Z)$. These assignments were confirmed by selective decoupling of the corresponding 8 doublets ($^2J(E, Z)$ 2.8—3.3 Hz). All other coupling constants were also determined by selective irradiations.

Deuteroboration of IIa followed by the cleavage of the C(2)—B bond by deuterated acid should give IIIa as sole product and bring another proof of the proposed stereochemistry of IIIa. This experiment was unsuccessful. Addition of B_2D_6 to IIa in THF formed the alkylborane, but no cleavage of the C—B bond could be observed on adding one equivalent of CD_3CO_2D, $CD_3CD_2CO_2D$ [14] or D_2SO_4 at 60°C. The complex decomposed at higher temperatures or upon addition of excess acid.

Regioselective protonation

Characterisation of the product obtained by protonation of Fe(η^4-diene)-$(CO)_3$ with noncoordinating acids has had a complicated history [15—18]. Protonation of Fe(η^4-diene)L_3 complexes (where L = phosphite [19] and phosphine [20] ligands) yields isolable species, and Brown et al. [21] reported recently a single crystal neutron and X-ray diffraction study of (η^3-C_8H_{13})Fe-$[P(OCH_3)_3]^+BF_4^-$. A significant finding of this study is the existence of a C—H···Fe two-electron three-center interaction. This interaction seems to

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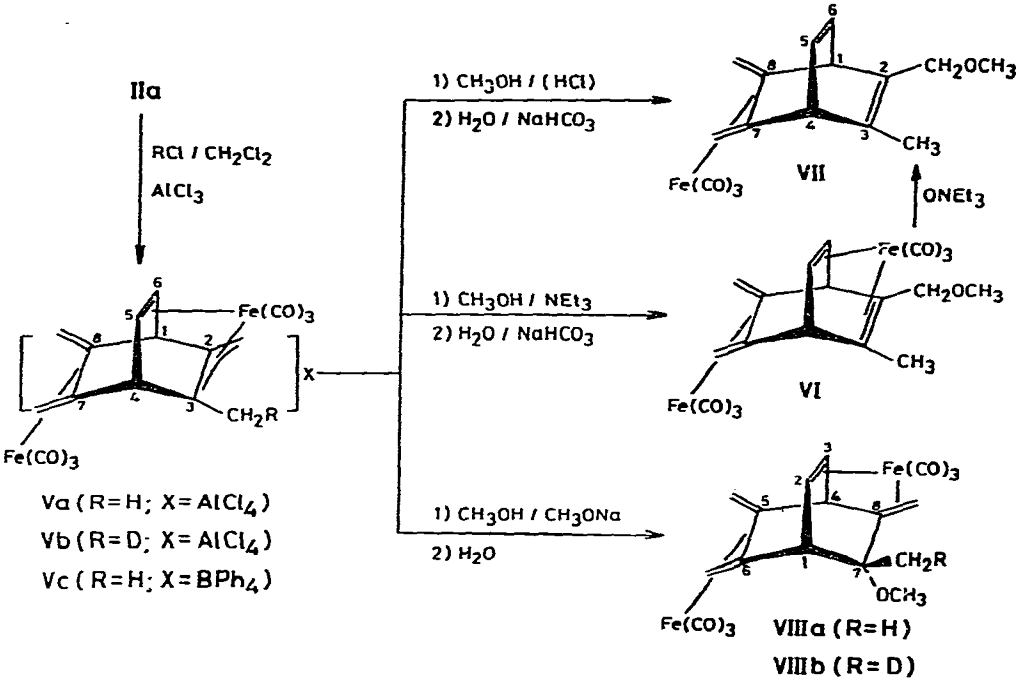
* Details of the new method of calculation of LIS data will be given in a forthcoming article [27].



SCHEME 2

relieve the coordinative and electronic unsaturation of the otherwise 16-electron Fe atom in a (η^3-enyl)FeL_3 cation whenever no other ligand is available for coordination.

In the present case, the endocyclic double bond of complex IIa may act as an extra ligand. It could possibly direct the protonation to one of the two *s-cis*-butadiene systems of the pentaene by stabilising only one of the two possible cations.

On adding one equivalent HCl to IIa in dichloromethane in the presence of $AlCl_3$, the tetrachloroaluminate salt of the η^3-dienyl cation Va separated as a yellow powder (Scheme 2). The ^{1}H and ^{13}C NMR spectra of the more stable BPh_4^- salt Vc (Fig. 2) do not vary up to 10° C (the compound decomposes at higher temperatures). There is no site exchange which would rapidly equilibrate the hydrogens on a terminal carbon atom on the NMR time scale. Protonation on one of the two diene systems is supported by the following evidence: (i) The ^{13}C signal of one terminal carbon atom (Table 7) is a quartet typical of a sp^3 C(methyl), and the H(10) signal is a singlet which integrates as 3 protons. The H(9) signals are two doublets with a geminal coupling constant of 2.4 Hz typical of a η^3-allyl group bonded to iron [22]. (ii) Addition of DCl to IIa gives Vb, and quenching of Vb in CH_3OD/CH_3ONa gives VIIIb whose ^{1}H NMR spectrum is identical with that of VIIIa, except for the "methyl" signal which now integrates as two protons. Thus, deuterium incorporation only occurred at one site. (iii) The ^{1}H and ^{13}C resonances attributable to the other diene systems of Vc, and of the products VI and VIIIa of its quenching in methanol, are typical

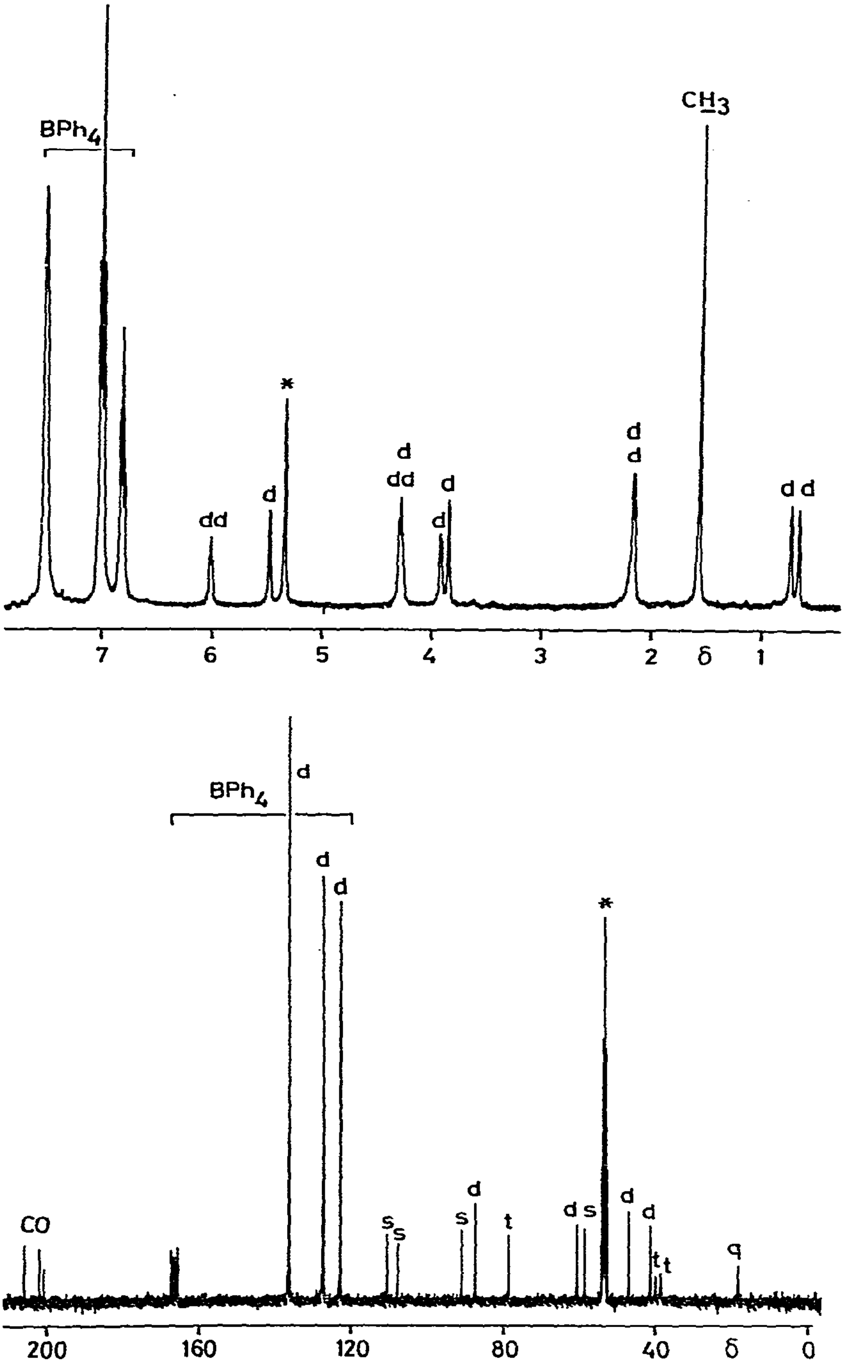


Fig. 2. 360 MHz ^1H NMR and 90.55 MHz ^{13}C NMR spectra of Vc in SO_2/CD_2Cl_2 (3/1) at −20°C (* = solvent).

TABLE 7

^{1}H and ^{13}C NMR PARAMETERS OF THE PRODUCTS OF PROTONATION OF IIa, AND OF QUENCHING OF Va [a]

	Vc [c]	VI	VII	VIII [d]	VIIIa [d]
H(1, 4) [b]	3.91, 4.29(2, d) [e]	4.25, 3.89(2, bd) [f]	4.48, 4.24(2, dd) [h]	H(1, 4) [b]	3.24(1, bs), 2.75(1, d) [i]
H(5, 6)	6.03, 4.26(2, dd)	3.45, 3.39(2, dd)	7.01(2, dd)	H(2, 3)	2.98(1, dd), 1.74(1, m)
H(9*E*)	5.49(1, d)	3.82(1, d) [g]	4.05(2, s)	H(9, 10*E*)	2.18, 2.10(2, d)
H(9*Z*)	3.84(1, d)	3.36(1, d) [g]		H(9, 10*Z*)	0.55, 0.54(2, d)
H(11, 12*E*)	2.16, 2.15(2, d)	1.82, 1.84(2, d)	2.15, 2.18(2, d)	H(12*E*)	1.33(1, d)
H(11, 12*Z*)	0.64, 0.72(2, d)	0.35, 0.36(2, d)	0.37(2, d)	H(12*Z*)	0.81(1, d)
CH_3	1.56(3, s)	1.79(3, s)	1.92(3, s)	CH_3	1.60(3, s)
OCH_3	—	3.40(s, s)	3.20(3, s)	OCH_3	3.85(3, s)
C(1, 4) [j]	47.5, [k] 41.8(d, 150)	49.2, 43.6(d, 150)	53.7, 49.8(d, 144)	C(1, 4) [j]	49.6, 46.8(d, 144)
C(2, 3)	59.1, 91.2(s)	72.0, 68.8(s)	144.6, 139.9(s)	C(2, 3)	58.3(d, 141), 16.2(d, 158)
C(5, 6)	87.6, 61.0(d, 181)	38.8, 39.4(d, 180)	139.1, 139.8(d, 177)	C(5, 6)	107.9, 111.8(s)
C(7, 8)	110.9, 108.1(s)	111.5, 111.8(s)	114.3, 116.0(s)	C(7, 8)	89.3, 87.3(s)
C(9)	78.8(t, 162)	70.7(t, 144)	68.5(t, 145)	C(9, 10)	38.2, 40.1(t, 160)
C(11, 12)	40.4, 39.1 [l] (t, 161)	37.2, 37.5(t, 159)	38.3(t, 161)	C(12)	29.9(t, 162)
CH_3	18.9(q, 125)	18.8(q, 128)	15.8(q, 128)	CH_3	19.8(q, 128)
OCH_3	—	58.7(q, 140)	57.1(q, 135)	OCH_3	54.9(q, 148)
CO	206.0, 202.1(s) 201.0(s)	215.6(s) 211.2(bs)	211.6(s)	CO	216.7, 210.1(s) 211.3(bs)

[a] The numbering scheme of complexes is given in Scheme 2. [b] ^{1}H NMR (360 MHz) data in SO_2/CD_2Cl_2 (3 : 1) at −20°C for Vc, in CD_2Cl_2 at room temperature for VI, VII and VIIIa. From left to right: δ in ppm relative to TMS, integration, multiplicity. [c] BPh_4^- ^{1}H signals: 7.53(8, m), 7.02(8, m), 6.83(4, m), ^3J(*meta, para*) 7.2 Hz; ^{13}C signals: 136.6, 127.6, 123.1(d, 159), 166.5(q, J(B, C) 49 Hz). [d] VIIIb has the same ^{1}H NMR spectrum as VIIIa apart from the resonance at 1.60 ppm which integrates as two protons. [e] Coupling constants ± 0.1 Hz: ^3J(H(1), H(6)) 5.7, ^3J(H(4), H(5)) 5.1, ^3J(H(5), H(6)) 4.8, $|^2J|$(H(9*E*), H(9*Z*)) 2.4, $|^2J|$(H(11*E*), H(11*Z*)) 2.9, $|^2J|$(H(12*E*), H(12*Z*)) 3.1. [f] ^3J(H1), H(6)) = ^3J(H(4), H(5)) 5.8, ^3J(H(5), H(6)) 5.0, ^4J(H(1), H(5)) 1.1, ^4J(H(4), H(6)) 1.2, $|^2J|$(H(11*E*), H(11*Z*)) 2.7. [g] Magnetically non-equivalent protons at room temperature with germinal coupling constant of 12 Hz. [h] ^3J(H(1), H(6)) = ^3J(H(4), H(5)) 3.5, ^3J(H(5), H(6)) 4.2, $|^2J|$(H(11*E*), H(11*Z*)) 2.7. [i] ^3J(H(1), H(2)) 0.9, ^4J(H(1), H(3)) 1.8, ^3J(H(2), H(3)) 4.4, ^3J(H(3), H(4)) 6.6, $|^2J|$(*E*, *Z*) 2.1, 2.6 and 1.8 for H(9), H(10) and H(12), respectively. [j] ^{13}C NMR (90.55 MHz) data in SO_2/CD_2Cl_2 (3 : 1) at −20°C for Vc, in $CDCl_3$ at room temperature for VI, VII and VIIIa, from left to right: δ in ppm relative to TMS, multiplicity, ^1J(C, H) in Hz. [k] ^3J(C, H) 6. [l] ^1J(C, H) 158.

of a "normal" (η^4-diene)Fe(CO)$_3$ system. The C(5)—C(6) endocyclic double bond is clearly bonded to the iron atom since the C(5) and C(6) doublets experience a high field shift of 52.6 and 79.2 ppm with respect to those of IIa. Thus, protonation has taken place on the η^4-diene bonded to the Fe(CO)$_3$ group in the *exo* position with respect to the roof-shaped ligand. This regioselectivity is due to the endocyclic double bond which is able to relieve coordinative and electronic unsaturation only for the (η^3-dienyl)Fe(CO)$_3$ (*exo*) cation. The non-equivalence of the C(5, 6) and H(5, 6) resonances indicates that the η^2-ene is asymmetrically bonded to iron. The positive charge of the cation is probably more delocalised onto C(5) than onto C(6), since the H(5) chemical shift is uncharacteristically high for a coordinated olefin. The corresponding torsion of the C(1)—C(6)—C(5)—C(4) bridge is evidenced by the non-equivalence of J(H(1),H(6)) and J(H(4),H(5)) (Table 7, note *e*; the assignment of H(1, 4, 5, 6) was based on selective irradiation experiments) and by the negligible coupling between H(1) and H(5), and between H(4) and H(6). In IIa where the bridge is planar (Table 5, plane II with numbering scheme of Fig. 1), these protons do indeed couple (Table 6, note *e*).

Quenching of Vc in methanol or of Va in methanol containing the amount of triethylamine needed to neutralise the formed HCl yields the bimetallic complex VI (Scheme 2). The analytical (Experimental) and NMR data (Table 7) indicate that VI is the bis(tricarbonyliron) complex of 2-methoxymethyl-3-methyl-7,8-bis(methylene)bicyclo[2.2.2]2,5-octadiene, formally resulting from a 1,4-addition of methanol to IIa. The Fe(CO)$_3$ group in the *endo* position is still bonded to a η^4-*cis*-butadiene system as the chemical shifts and coupling constants of C(7, 8, 11, 12) are quite similar to those of IIa. The Fe(CO)$_3$ group in the *exo* position is now bonded to the two C—C double bonds of a substituted 1,4-hexadiene. Indeed, the C(2, 3) resonances of VI are shifted upfield by 41.3 and 44.5 ppm relative to the C(5, 6) signals of IIa, and the C(5, 6) doublets are shielded by ca. 101 ppm relative to the C(2, 3) signals of IIa. A comparable example, the η^6-W(CO)$_3$ complex of the pentaene I, has been reported previously [1]. In this complex, the endocyclic double bond must be coordinated to the metal atom, and the corresponding ^{13}C resonances are shielded by ca. 91 ppm. Two doublets are observed at room temperature for the H(9) protons, indicating that rotation about the C(2)—C(9) bond is blocked on the NMR time scale by the presence of the bulky Fe(CO)$_3$ group. We found no comparable behaviour in (1,4-hexadiene)Fe(CO)$_3$ chemistry.

On quenching Va in methanol, half of the metal content is lost. Addition of a tetrachloroaluminate salt in methanol liberates HCl, and forms the monometallic complex VII, probably by oxidative-addition of HCl on the Fe(CO)$_3$ (*exo*) group of VI followed by decomplexation. VII was also obtained by oxidation of VI with one equivalent ONEt$_3$ in acetone. Similar stereoselective oxidations of bimetallic complexes of I have been reported elsewhere [2].

Quenching of Va or Vc in strongly basic media (CH$_3$OH/CH$_3$ONa) yielded the bimetallic complex VIIIa (80%) (Scheme 2). The analytical and NMR data (Table 7) indicate that VIIIa is the bis(tricarbonyliron) complex of 7-methoxy-7-methyl-5,6,8-tris(methylene)bicyclo[2.2.2]oct-2-ene formally resulting from a 1,2-addition of methanol to IIa. Hydrogen scrambling is presumably absent, since quenching of Vb in CH$_3$OD/CH$_3$ONa yielded VIIIb, the product of a formal 1,2-addition of CH_3OD to IIa. The molecule is asymmetric with one $Fe(CO)_3$ group bonded to a η^4-*cis*-butadiene system (C(5, 6, 9, 10)). The other $Fe(CO)_3$ group, which must be in the *exo* position, is clearly bonded to the endocyclic double bond C(2)—C(3). The important difference between the upfield shifts of C(2) (91.9 ppm) and C(3) (124.0 ppm) relative to those of IIa, as well as the difference between the related *J*'s of H(1, 2, 3, 4) indicate again a torsion of the C(10)—C(2)—C(3)—C(4) bridge in VIIIa. The $Fe(CO)_3$ group (*exo*) is also bonded to C(8)—C(12), since the strong shielding of the C(12), H(12*E*) and H(12*Z*) resonances is indicative of a η^2-coordinated double bond. The *endo* position of the methoxy group of VIIIa is not proved as nuclear overhauser enhancement NOE experiments were inconclusive, but is the position expected for a *trans* nucleophilic attack on a (η^3-dienyl)$Fe(CO)_3$ cation [23]. To our knowledge, VIIIa is the first example of a (η^4-diene)$Fe(CO)_3$ complex in which the metal is bonded to two C—C double bonds in *gauche* positions with respect to each other.

In conclusion, stereospecific functionalisations of the *endo*,*exo*-5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene-bis(tetrahaptotricarbonyliron) (IIa) can be achieved. Hydrogenation and hydroboration of the uncoordinated double bond (C(2, 3)) occur onto its less hindered face. Contrastingly, proton addition occurs preferentially onto the *exo*-(diene)$Fe(CO)_3$ system because of the extra stabilization brought by coordination of the endocyclic double bond to the corresponding methylallyl-$Fe(CO)_3$ cation [3]. Such a stabilization (formation of a coordinatively saturated allyl-$Fe(CO)_3$ cation) is impossible without an external ligand if protonation had occurred onto the *endo*-(diene)$Fe(CO)_3$ of IIa. This feature makes the bimetallic complex IIa a useful starting material for the stereospecific preparations of complicated bicyclic systems.

Experimental

All reactions were carried out under argon and the solvents were dried and degassed by standard methods [24]. Mass spectra at 70 eV were measured with a Hewlett-Packard GC-MS5980; IR spectra with a Perkin-Elmer 577 spectrophotometer; ^1H NMR spectra at 80 MHz (CW) and 360 MHz (FT) with Bruker WP-80 and WP-360 spectrometers; ^{13}C NMR spectra at 15.08 and 90.55 MHz with Bruker WP-60 and WP-360 spectrometers and using a deuterium lock. E. Manzer (Mikrolabor, ETH, Zürich) carried out the microanalyses.

The preparation of 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (I) has been described elsewhere [25], as well as the reaction of I with iron carbonyls [1], and the preparation of IIIb [11]. An improved synthesis of IIa is given here: $Fe_2(CO)_9$ (45 g) and I (7 g) were heated at 45°C in n-hexane (500 ml)/methanol (50 ml) under a stream of argon for 30 h. Acid alumina grade I (150 g) was then added to the filtered green solution to decompose $Fe_3(CO)_{12}$. The suspension was filtered, washed with diethyl ether, and the filtrate evaporated to dryness (caution: the $Fe(CO)_5$ formed must be collected in a liquid nitrogen trap during this operation). The brown crystalline mass was recrystallised from n-heptane at —10°C giving IIa (10 g, 51%) and IIb [1] (0.5 g, 2.5%). The mother liquor containing $(C_{12}H_{12})Fe(CO)_3$ [1] (2.5 g, 19%) was recycled with fresh $Fe_2(CO)_9$ as above. Overall yield in IIa: 63%.

Deuteration of IIa

n-Hexane (30 ml) and CD_3OD (1 ml) were transferred on a vacuum line into a flask containing IIa (0.250 g) and dry PtO_2 (0.05 g). The suspension was stirred for 2 days under D_2 (1 atm), then filtered and evaporated to dryness. The yellow residue was taken up in n-hexane and recrystallised at —25° C, giving IIIa (0.245 g, 97%). The same reaction under H_2 gave IIIb. No deuteration of the *diexo* isomer IIb was observed under the same conditions.

IIIb: Yellow air stable crystals. M.p. 92—94° C. Mass spectrum (MS) (peaks corresponding to ^{56}Fe): 440 (7, M^+), 412 (42), 384 (61), 356 (28), 328 (11), 300 (100), 272 (58) (successive loss of 6 CO), 56 (Fe^+). Anal. Found: C, 49.21. $C_{18}H_{12}D_2O_6Fe_2$ calcd.: C, 49.13%. A deuterium content of 95% was calculated by comparison of the relative MS intensities of the molecular peak envelope (434—440) with that of the undeuterated complex IIIb after correction for ^{13}C. IR (n-hexane): $\nu(CO)$ 2060, 2058, 1985, 1983(sh), 1974 and 1966 cm^{-1}.

Hydroboration of IIa

To a solution of complex IIa (2.4 g, 5.5 mmol) in THF (30 ml) at 0° C was added $NaBH_4$ (0.8 g), then, dropwise, a solution of $Et_2O \cdot BF_3$ (2 g, 14.1 mmol), and the mixture stirred for 4 h at room temperature. Water (1.6 g) was added dropwise to the solution cooled in an ice bath, then KOH 3 *M* (1.6 g) and finally H_2O_2 (30%, 3 g). The resulting mixture was stirred at 20° C for 16 h, filtered and extracted with H_2O (30 ml)/CH_2Cl_2 (3 × 30 ml). The dichloromethane extracts were dried over $MgSO_4$, and evaporated to dryness. TLC and ^1H NMR of the residue revealed the presence of a single product. Recrystallisation from CH_2Cl_2/n-hexane at —25° C gave complex IV (2.2 g). Yield 87%.

Attempts to prepare IIIa through deuteroboration of IIa using B_2D_6/THF failed as the C—B bond formed could not be cleaved by CH_3CO_2D, $CH_3CH_2CO_2D$ [14], CF_3CO_2D or D_2SO_4 at 60° C. An attempt to prepare a trialkylborane was unsuccessful as the borabicyclononane BBH [26] did not react with IIa.

IV: Yellow crystals. M.p. 160—162° C. Anal. Found: C, 48.36; H, 3.39. $C_{18}H_{14}O_7Fe_2$ calcd.: C, 47.62; H, 3.11%. Mass spectrum: 454 (5, M^+), 426 (33), 398 (48), 370 (30), 342 (15), 314 (100), 286 (78) (successive losses of 6 CO), 56 (Fe^+). IR: $\nu(CO)$ 2052, 1983, 1971 and 1967 cm^{-1} in n-hexane; $\nu(OH)$ 3605 cm^{-1} in CCl_4. UV (isooctane): 311(sh) (2420), 221 nm (20 900 M^{-1} cm^{-1}).

Protonation of IIa

Freshly sublimed iron-free $AlCl_3$ (Fluka AG) (0.17 g) was added to a solution of IIa (0.5 g) in anhydrous dichloromethane (15 ml). HCl (25 ml) was injected through a serum cap into the solution which turned orange. Stirring was continued for 2 h while a yellow microcrystalline powder precipitated out. Addition of n-hexane (15 ml), filtration and drying in vacuo gave Va (0.593 g, 85%). Va contained a paramagnetic impurity which could not be eliminated by recrystallisation as it is insoluble or decomposes immediately in most solvents or in a few minutes in nitromethane.

Va: Yellow powder. Anal. Found: C, 34.25; H, 2.14; Cl, 22.96. $C_{18}H_{13}O_6Fe_2AlCl_4$ calcd.: C, 35.69; H, 2.16; Cl, 23.41%. IR (Nujol): $\nu(CO)$ 2119, 2062, 1985, 1969(sh) and 1962 cm^{-1}. The same reaction using DCl (25 ml) gave Vb

(0.6 g, 85%) which contained also a paramagnetic impurity (same microanalyses and IR spectrum as Va).

A solution of $NaBPh_4$ (0.5 mmol) in CH_3NO_2 (2 ml) was rapidly added to Va (0.15 g, 0.248 mmol) dissolved in the minimum amount of CH_3NO_2. Filtration of a first crop of microcrystals after 10 min gave Vc (0.063 g, 33%) free from paramagnetic impurities.

Vc: Yellow microcrystals unstable in the air and upon warming. Anal. Found: C, 66.31; H, 4.55. $BC_{42}H_{33}O_6Fe_2$ calcd.: C, 66.71; H, 4.40%. IR (KBr): ν(CO) 2105, 2060, 2050(sh), 1987 and 1959 cm^{-1}.

Quenching of Va

(a) Va (0.5 g, 0.825 mmol) was vigorously stirred in methanol (10 ml) containing triethylamine (3.3 mmol). After 15 sec the mixture was rapidly poured into ether (100 ml)/water (100 ml), and the ether extracts were dried over $MgSO_4$ and evaporated to a small volume. Chromatography on a 40 X 2 cm column packed with silica gel using n-hexane/dichloromethane (1/1) as eluent gave a yellow band which yielded VI (0.186 g, 35%) after recrystallisation from n-hexane at —25°C.

VI: Yellow crystals. M.p. 95°C. Anal. Found: C, 48.90; H, 3.45. $C_{19}H_{16}O_7Fe_2$ calcd.: C, 48.76; H, 3.45%. Mass spectrum: 468 (0.5, M^+), 440 (3, $M^+ -$ CO), 412 (32, $M^+ - 2$ CO), 384 (22, $M^+ - 3$ CO), 356 (1, $M^+ - 4$ CO), 354 (1), 352 (2), 328 (12, $M^+ - 5$ CO), 300 (100, $M^+ - 6$ CO), 272 (15), 270 (29), 268 (27), 56 (Fe^+). IR (n-hexane): ν(CO) 2063, 2042, 1984, 1968 and 1956(sh) cm^{-1}.

(b) Va (0.5 g) was stirred in methanol (50 ml, with or without added HCl), and the same workup as in (a) gave VII (0.135 g, 50%) after recrystallisation from n-hexane at —25°C.

VII: Yellow crystals. M.p. 41—43°C. Anal. Found: C, 58.41; H, 4.83. $C_{16}H_{16}O_4Fe$ calcd.: C, 58.56; H, 4.91%. Osmometry : molecular mass 325 ± 10. IR (n-hexane): ν(CO), 2060, 1979 and 1965 cm^{-1}. Oxidation of VI by one equivalent of $ONEt_3$ in benzene gave VII as major product (78%).

(c) Va (0.5 g) was stirred at 0°C in methanol (50 ml) containing t-BuOK (1 g) (or CH_3ONa) for 10 min, and the mixture extracted with water (100 ml)/ ether (100 ml) (dichloromethane should not be used). The ether extracts were dried over $MgSO_4$, and evaporated to a small volume. Chromatography on a 40 X 2 cm water cooled column packed with Florisil using n-hexane/CH_2Cl_2 (2/1) at 10°C gave a yellow band which yielded VIIIa (0.31 g, 80%) after recrystallisation from n-hexane at —25°C.

VIIIa: Crystals of rusty color. M.p. 190°C (dec.). Anal. Found: C, 48.80; H, 3.40. $C_{19}H_{16}O_7Fe_2$ calcd.: C, 48.76; H, 3.45%. Mass spectrum: 468 (2, M^+), 440 (21), 412 (34), 384 (3), 356 (55), 328 (100), 313 (31), 300 (24) (successive losses of 6 CO), 298 (33), 296 (42), 294 (26), 56 (Fe^+). IR (CCl_4): ν(CO) 2060, 1997, 1981, 1969 and 1932 cm^{-1}.

The same reaction starting with Vb and using deuterated methanol and CH_3ONa gave VIIIb (80%).

VIIIb: Same m.p. and IR spectrum as VIIIa. Anal. Found: C, 48.68; D + H, 3.54. $C_{19}DH_{15}O_7Fe_2$ calcd.: C, 48.66; D + H, 3.65%. Mass spectrum: 469 (<1, M^+), 441 (52), 413 (76), 385 (6), 357 (60), 329 (100), 314 (24), (successive losses of 6 CO), 301 (20), 299 (28), 297 (40), 56 (Fe^+).

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