156. Crystal and Molecular Structure of Tricarbonyl-[(1*R**,4*S**,4a*S**,9a*R**)-1,4-epoxy-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene]iron

by **Mauro Alini, Raymond Roulet**(1)

Institut de chimie minérale et analytique de l'Université, 3, place du Château, CH-1005 Lausanne

and **Gervais Chapuis**

Institut de cristallographie de l'Université, BSP-Dorigny, CH-1015 Lausanne

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Summary

The thermal cyclodimerization of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene assisted by $Fe_2(CO)_9$ gives the title complex **1**, a precursor for the synthesis of antitumoral anthracyclinones. The crystal structure of **1** has been determined by X-ray diffraction: $a = 11.188$ (1); $c = 26.968$ (3) Å; space group tetragonal, $P4_12_12$, $Z = 8$; $R = 0.041$; $R_w = 0.033$. The tricarbonyliron group is in the *exo*-position and the coordination polyhedron is tetragonal pyramidal. The NMR coupling constants are well-related to the observed dihedral angles between the non-aromatic protons and now give a reliable criterion for assigning the stereochemistry of the metal in d^8-complexes of 2,3-dimethylidene-7-oxanorbornane derivatives.

Introduction. – We reported recently [1] the first example of a formal [4+2]-cycloaddition of a 1,3-diene to a C,C double bond assisted by iron-carbonyls, *i.e.* the thermal cyclodimerization of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene in the presence of $Fe_2(CO)_9$ in MeOH giving the title product. The same reaction occurs with lower yields in the presence of $Ru_3(CO)_{12}$ and can be rendered catalytically in the presence of $Os_3(CO)_{12}$ [2]. We report here on the molecular structure of the cycloadduct tricarbonyl[(1*R**,4*S**,4a*S**,9a*R**)-1,4-epoxy-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene]iron (**1**) which can serve as a structural basis for the d^8-complexes of this potential antitumoral anthracyclinone precursor.

Determination of the Structure of 1. – Crystals of **1** were grown by slow cooling of a solution in hexane to −25°. Single-crystal diffraction intensities were collected on a *Syntex P2₁* autodiffractometer. The crystal habit was a prism delimited by the eight faces (±1, ±1, 0) and (0, 0, ±1); owing to the asymmetric

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(1) Author to whom correspondence should be addressed.

Table 1. *Summary of Crystal Data, Intensity Collection and Refinement*

Formula	$C_{19}H_{16}O_4Fe$	Radiation	Mo-K_α, Nb filtered ($\lambda = 0.71069$ Å)
Molecular mass	364.18	Min. & max. transmission	1.193 and 1.221
Dimensions (mm)		Scan method	$2\theta - \theta$
Crystal system	Tetragonal	Background from	Scan profile interpretation [9]
Space group	$P4_12_12$	$(\sin\theta/\lambda)_{max}$	0.651
a (Å)	11.188 (1)	Data collected	$h, k, \pm l; k > h$
c (Å)	26.968 (3)	No. of unique reflections	2320
V (Å^3)	3375.6 (1)	No. of reflections ($I < 3\sigma$)	922
Z	8	No. of reflections/ No. of parameters	10.65
d_{obs} (g cm^{-3})	1.43 (1) (ZnI_2 solution)	Resolution method	*Patterson* and *Fourier*
d_{calc} (g cm^{-3})	1.433	Refinement method	Block-diagonal least-squares
F_{000}	1504	Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Systematic extinctions	$h00$: $h = 2n+1$	w	l/σ^2
	$0k0$: $k = 2n+1$	R	0.041
	$00l$: $l = 2n+1$	R_w	0.033
μ (cm^{-1})	9.0	Goodness of fit	1.98

shape of the crystal, an absorption correction based on the *Gaussian* integration method was applied. *Table 1* gives the crystallographic data and data-collection procedure; the X-Ray 72 System of programs [3] was used. Atomic scattering factors calculated by *Cromer & Mann* [4] were assigned to the neutral non-H-atoms. For H-atoms the values calculated by *Stewart et al.* [5] were introduced in the structure factor calculations. Anomalous dispersion corrections [6] were applied to Fe-atoms which were located from the *Patterson* map, and the remaining non-H-atoms could be identified on successive *Fourier* maps. A difference *Fourier* synthesis resulting from an anisotropic refinement of the non-H-atoms revealed 10 of the 16 H-atoms. At this stage of refinement the two possible space groups were discriminated on the basis of the best R-ratio: $R = 0.066$ ($P4_32_12$) and $R = 0.054$ ($P4_12_12$). The space group $P4_12_12$ was adopted and the aromatic ring atoms were excluded from further refinement to keep an optimal ratio between experimental

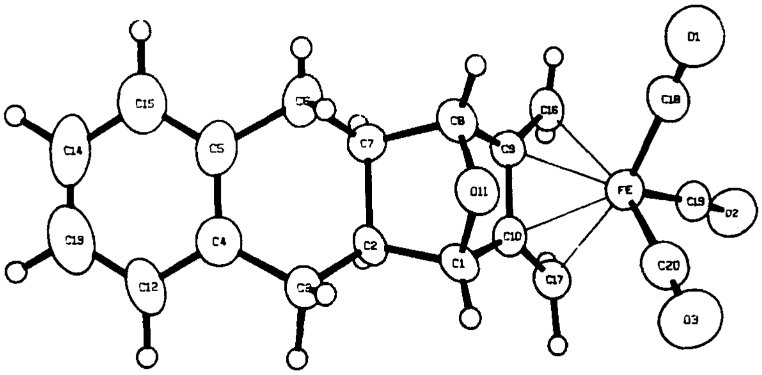

Figure. *A perspective view of the molecular structure of* **1**

Table 2. *List of Atomic Parameters for Complex* **1**. 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. The e.s.d. of the last significant digit is in parentheses.

Atom	X	Y	Z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.12581 (6)	0.04440 (6)	0.09416 (2)	0.0394 (4)	0.0475 (4)	0.0388 (3)	0.0018 (4)	−0.0010 (4)	−0.0004 (4)
O(1)	0.1001 (4)	0.2714 (3)	0.0418 (1)	0.106 (3)	0.058 (3)	0.081 (3)	0.001 (3)	−0.021 (2)	0.020 (2)
O(2)	0.4578 (3)	0.3632 (3)	0.2268 (1)	0.080 (3)	0.074 (3)	0.064 (2)	−0.011 (2)	−0.018 (2)	0.032 (2)
O(3)	0.3849 (3)	0.0461 (4)	0.0784 (1)	0.040 (2)	0.107 (3)	0.095 (3)	−0.002 (3)	−0.001 (2)	−0.002 (2)
C(1)	0.2356 (4)	0.0873 (4)	0.2006 (2)	0.031 (3)	0.042 (3)	0.047 (3)	0.003 (3)	−0.005 (2)	0.004 (2)
C(2)	0.1808 (4)	0.1041 (5)	0.2520 (2)	0.036 (3)	0.051 (4)	0.032 (3)	−0.005 (3)	−0.005 (2)	0.001 (3)
C(3)	0.2728 (4)	0.1423 (5)	0.2917 (2)	0.042 (3)	0.057 (4)	0.042 (3)	−0.001 (3)	0.002 (3)	0.003 (3)
C(4)	0.2137	0.2025	0.3348	0.0406	0.0446	0.0558	−0.0120	−0.0076	−0.0040
C(5)	0.1320	0.2940	0.3239	0.0524	0.0559	0.0506	−0.0186	0.0080	−0.0131
C(6)	0.1074 (6)	0.3174 (5)	0.2708 (2)	0.061 (4)	0.045 (4)	0.048 (3)	0.009 (4)	−0.006 (3)	−0.006 (3)
C(7)	0.0851 (4)	0.2019 (4)	0.2408 (2)	0.024 (3)	0.047 (3)	0.043 (3)	−0.003 (3)	0.001 (2)	−0.005 (3)
C(8)	0.1018 (4)	0.2200 (4)	0.1850 (2)	0.049 (3)	0.025 (3)	0.042 (3)	0.000 (3)	−0.013 (2)	0.000 (2)
C(9)	0.0567 (4)	0.1088 (4)	0.1596 (1)	0.031 (3)	0.050 (3)	0.033 (2)	0.003 (2)	−0.001 (2)	−0.003 (2)
C(10)	0.1446 (4)	0.0220 (4)	0.1694 (1)	0.049 (3)	0.037 (3)	0.033 (2)	−0.001 (3)	0.005 (2)	−0.003 (2)
C(12)	0.2363	0.1724	0.3839	0.0610	0.0804	0.0405	−0.0165	−0.0025	−0.0035
C(13)	0.1810	0.2371	0.4215	0.0869	0.0982	0.0477	−0.0334	−0.0055	−0.0064
C(14)	0.1007	0.3217	0.4114	0.0696	0.1014	0.0568	−0.0199	0.0123	−0.0348
C(15)	0.0759	0.3531	0.3628	0.0612	0.0553	0.0623	−0.0084	−0.0028	−0.0103
C(16)	−0.0426 (7)	0.0786 (5)	0.1294 (2)	0.047 (5)	0.086 (3)	0.025 (3)	0.011 (4)	−0.010 (3)	0.000 (3)
C(17)	0.1384 (6)	−0.0934 (5)	0.1485 (2)	0.059 (4)	0.043 (3)	0.042 (3)	0.014 (3)	−0.001 (3)	0.003 (3)
C(18)	0.1112 (5)	0.1822 (5)	0.0615 (2)	0.057 (4)	0.057 (4)	0.039 (3)	0.001 (3)	−0.002 (3)	−0.003 (3)
C(19)	0.0743 (4)	−0.0642 (5)	0.0496 (2)	0.054 (4)	0.088 (4)	0.037 (3)	0.022 (3)	0.007 (3)	0.002 (3)
C(20)	0.2822 (5)	0.0446 (5)	0.0837 (2)	0.058 (4)	0.058 (4)	0.051 (3)	0.001 (3)	−0.003 (3)	0.001 (3)
H(1)	0.321 (3)	0.066 (3)	0.200 (1)	0.02 (1)					
H(2)	0.143 (3)	0.039 (3)	0.262 (1)	0.02 (1)					
H(3X)	0.338 (4)	0.188 (4)	0.274 (1)	0.08 (2)					
H(3N)	0.326 (3)	0.064 (3)	0.297 (1)	0.04 (1)					
H(6N)	0.060 (3)	0.373 (3)	0.263 (1)	0.02 (1)					
H(6X)	0.180 (3)	0.358 (3)	0.253 (1)	0.04 (1)					
H(7)	0.015 (3)	0.182 (4)	0.247 (1)	0.04 (1)					
H(8)	0.084 (3)	0.295 (3)	0.167 (1)	0.05 (1)					
H(12)	0.2954	0.0979	0.3925	0.0700					
H(13)	0.2036	0.2175	0.4600	0.0700					
H(14)	0.0537	0.3679	0.4409	0.0700					
H(15)	0.0136	0.4271	0.3539	0.0700					
H(16*Z*)	−0.070 (5)	0.007 (5)	0.133 (2)	0.07 (2)					
H(16*E*)	−0.093 (3)	0.134 (4)	0.118 (1)	0.07 (1)					
H(17*Z*)	0.066 (4)	−0.133 (4)	0.149 (2)	0.07 (2)					
H(17*E*)	0.217 (5)	−0.151 (5)	0.154 (2)	0.07 (2)					

Table 3. *Bond Lengths (Å) in* **1**. The e.s.d. of the last significant digit is given in parentheses. The phenyl ring distances are not reported.

Fe–C(18)	1.783 (5)	C(8)–C(9)	1.508 (6)	C(3)–H(3X)	1.01 (4)
Fe–C(19)	1.803 (5)	C(9)–C(10)	1.407 (6)	C(3)–H (3N)	1.06 (3)
Fe–C(20)	1.772 (6)	C(10)–C(1)	1.508 (6)	C(6)–H(6X)	1.04 (3)
Fe–C(9)	2.056 (4)	C(1)–O(11)	1.443 (5)	C(6)–H(6N)	0.84 (4)
Fe–C(10)	2.056 (4)	C(2)–C(7)	1.560 (7)	C(7)–H(7)	0.83 (4)
Fe–C(16)	2.144 (7)	C(8)–O(11)	1.457 (5)	C(8)–H(8)	0.99 (4)
Fe–C(17)	2.132 (5)	C(9)–C(16)	1.417 (8)	C(16)–H(16*Z*)	0.86 (6)
C(1)–C(2)	1.528 (6)	C(10)–C(17)	1.410 (7)	C(16)–H(16*E*)	0.88 (4)
C(2)–C(3)	1.545 (6)	C(18)–O(1)	1.137 (6)	C(17)–H(17*Z*)	0.92 (5)
C(3)–C(4)	1.496 (5)	C(19)–O(2)	1.139 (6)	C(17)–H(17*E*)	1.10 (5)
C(5)–C(6)	1.481 (5)	C(20)–O(3)	1.157 (7)		
C(6)–C(7)	1.544 (7)	C(1)–H(1)	0.99 (3)	Fe...O(11)	3.186 (4)
C(7)–C(8)	1.527 (6)	C(2)–H(2)	0.83 (3)	C(16)...C(17)	2.840 (9)

Table 4. *Bond Angles (°) in* **1**. The e.s.d. of the last significant digit is given in parentheses. The phenyl ring angles are not reported.

C(18)–Fe–C(19)	102.9 (2)	C(1)–C(10)–C(17)	134.4 (4)
C(18)–Fe–C(20)	90.6 (2)	C(9)–C(10)–C(17)	121.4 (4)
C(19)–Fe–C(20)	102.2 (2)	H(1)–C(1)–C(2)	115 (1)
Fe–C(18)–O(1)	177.3 (3)	H(1)–C(1)–C(10)	122 (2)
Fe–C(19)–O(2)	177.2 (2)	H(1)–C(1)–O(11)	105 (2)
Fe–C(20)–O(3)	178.1 (4)	H(2)–C(2)–C(1)	111 (2)
C(9)–Fe–C(10)	40.0 (1)	H(2)–C(2)–C(3)	109 (2)
C(9)–Fe–C(16)	39.4 (2)	H(2)–C(2)–C(7)	108 (2)
C(10)–Fe–C(17)	39.3 (2)	H(3X)–C(3)–C(2)	107 (2)
C(2)–C(1)–C(10)	107.1 (4)	H(3X)–C(3)–C(4)	117 (2)
C(2)–C(1)–O(11)	101.9 (4)	H(3X)–C(3)–H(3N)	94 (3)
C(10)–C(1)–O(11)	102.6 (3)	H(3N)–C(3)–C(2)	104 (2)
C(3)–C(2)–C(1)	113.2 (4)	H(3N)–C(3)–C(4)	120 (2)
C(3)–C(2)–C(7)	113.4 (4)	H(6X)–C(6)–C(5)	112 (2)
C(2)–C(3)–C(4)	111.5 (3)	H(6X)–C(6)–C(7)	104 (2)
C(3)–C(4)–C(5)	117.0 (2)	H(6X)–C(6)–H(6N)	93 (3)
C(3)–C(4)–C(12)	123.3 (2)	H(6N)–C(6)–C(5)	118 (2)
C(4)–C(5)–C(6)	116.8 (2)	H(6N)–C(6)–C(7)	113 (2)
C(6)–C(5)–C(15)	124.2 (2)	H(7)–C(7)–C(8)	110 (2)
C(5)–C(6)–C(7)	112.9 (4)	H(7)–C(7)–C(2)	115 (3)
C(2)–C(7)–C(6)	111.9 (4)	H(7)–C(7)–C(6)	105 (3)
C(2)–C(7)–C(8)	101.5 (4)	H(8)–C(8)–C(7)	125 (2)
C(6)–C(7)–C(8)	112.6 (4)	H(8)–C(8)–C(9)	114 (2)
C(7)–C(8)–C(9)	107.4 (4)	H(8)–C(8)–O(11)	104 (2)
C(7)–C(8)–O(11)	100.7 (3)	H(16*Z*)–C(16)–C(9)	116 (3)
C(9)–C(8)–O(11)	102.4 (3)	H(16*Z*)–C(16)–H(16*E*)	117 (4)
C(8)–C(9)–C(10)	104.4 (3)	H(16*E*)–C(16)–C(9)	121 (3)
C(8)–C(9)–C(16)	136.1 (4)	H(17Z)–C(17)–C(10)	118 (3)
C(10)–C(9)–C(16)	119.5 (4)	H(17*Z*)–C(17)–H(17*E*)	114 (4)
C(1)–C(10)–C(9)	104.0 (4)	H(17*E*)–C(17)–C(10)	116 (2)

observations and variables. Subsequent refinement with isotropic thermal coefficients for H-atoms gave a final $R = 0.041$. The final positional and thermal parameters are listed in *Table 2*[2]. Bond distances 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, prepared by the program ORTEP [7] is given in the *Figure* where the numbering scheme is indicated.

Discussion. – The structure is composed of discrete molecules of **1**; all intermolecular contacts are equal to or greater than the sum of *van der Waals* radii. Each molecule possesses an approximate mirror plane VIII *(Table 5)* which passes through the Fe-atom, one CO-group and the middle of the C(2)–C(7) bond.

Table 5. *Least-squares Planes in* **1**

	Atoms defining plane	Equation of mean plane
Plane I	C(9,10,16,17)	$-5.665X - 3.500Y + 21.670Z = 2.765$
Plane II	C(1,8,9,10)	$-5.494X - 2.947Y + 22.392Z = 2.937$
Plane III	C(1,8), H(1,8), O(11)	$1.217X + 4.617Y + 24.388Z = 5.598$
Plane IV	C(1,2,7,8)	$7.477X + 8.050Y + 5.079Z = 3.477$
Plane V	C(2,3,6,7)	$-6.595X - 3.968Y + 19.570Z = 3.337$
Plane VI	C(3-6,12-15)	$8.232X + 7.575Y + 0.265Z = 3.382$
Plane VII	C(18,20), a, b[a]	$4.803X + 7.730Y + 15.684Z = 2.960$
Plane VIII	C(19), O(2,11), Fe, c, d, e	$6.481X - 8.698Y + 6.602Z = 1.163$

Displacement of atoms from mean plane (Å)

Plane I		Plane II		Plane III		Plane IV	
C(9)	−0.010	C(1)	0.002	C(1)	−0.016	C(1)	0.005
C(10)	0.010	C(8)	−0.002	H(1)	−0.023	C(2)	−0.007
C(16)	0.005	C(9)	0.003	C(8)	0.054	C(7)	0.007
C(17)	−0.005	C(10)	−0.003	H(8)	−0.063	C(8)	−0.005
				O(11)	0.048		

Plane V		Plane VI		Plane VII		Plane VIII	
C(2)	−0.011	C(3)	0.018	C(18)	−0.053	C(19)	0.205
C(3)	0.006	C(4)	−0.001	C(20)	0.053	O(2)	0.143
C(6)	−0.006	C(5)	0.016	a	0.064	O(11)	−0.273
C(7)	0.011	C(6)	−0.023	b	−0.064	Fe	−0.112
		C(12)	−0.030			c	−0.005
		C(13)	0.014			d	−0.027
		C(14)	−0.008			e	0.070
		C(15)	0.013				

Dihedral angle between planes (°)

I-II 3.3; I-VII 88.0; I-VIII 81.6; II-III 126.1; II-VIII 82.9; III-IV 122.7; III-VIII 87.9; IV-V 120.8; IV-VIII 82.7; V-VI 131.8; V-VIII 83.5; VI-VIII 84.4

[a] a, b, c, d, e are the midpoints of bonds C(17)–C(10), C(16)–C(9), C(2)–C(7), C(4)–C(5) and C(13)–C(14), respectively.

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

The arrangement of ligands about the Fe-atom is tetragonal pyramidal. The basal coordination sites are occupied by two CO-groups and the midpoints of the outer C,C-bonds of the diene system. The apex-to-base angles are 102.5 (3) for the CO-groups and 112° for the C,C-bond midpoints. The basal angles are 90.6 (2), 93 and 65°, the smallest angle being 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 9° with the normal to the basal plane. The three diene C,C-distances are equal within σ and the sum of angles at the 'inner' C-atoms is 360.0 (5)°. In contrast, the H(*Z*)- and H(*E*)-atoms are not coplanar with the diene C-atoms. The H(*Z*) atoms deviate from the diene plane away from the metal by 40° and the H(*E*) atoms are bent towards the metal by 11°. These values are in agreement with the mean deviations found from a statistical comparison of seven (1,3-diene)$Fe(CO)_3$ structures [8]. Deviation of the H(*E*)-atoms towards the *exo*-side of the roof-shaped ligand reduces sharply the dihedral angle between bonds C(8)–H(8) and C(16)–H(16*E*), contrary to the *endo*-$Fe(CO)_3$ isomer. This is reflected in the ^{1}H-NMR spectrum of **1** [1]: the H(*E*) signal exhibits a supplementary coupling with $J(8,16E) = 0.8$ Hz which is absent in the spectrum of the *endo*-isomer. Thus, the observation of a ^4J-coupling in the ^{1}H-NMR spectrum of one of the two stereoisomers should be a reliable criterion for assigning the stereochemistry of the metal in d^8-complexes of 2,3-dimethylidene-7-oxanorbornane derivatives. Finally, the observed dihedral angles between bonds C(6)–H(6X) and C(7)–H(7) (20°) and between C(6)–H(6N) and C(7)–H(7) (121°) are in agreement with the ^{1}H-NMR assignments reported earlier and give a firm basis to ^{1}H-NMR structural deductions concerning further transformations of ring B of this interesting precursor.

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