226. Crystal Structure and Absolute Configuration of (+)-(1*S*,2*R*)-5,6-Dimethylidene-2*exo*-norbornyl-*exo*-irontricarbonyl *p*-Bromobenzoate

by **Charles Barras, Raymond Roulet**[1])

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

Eric Vieira, Pierre Vogel[1])

Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005 Lausanne

and **Gervais Chapuis**

Institut de cristallographie de l'Université, BSP Dorigny

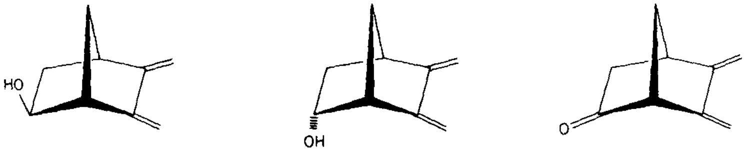
(8.VII.81)

Summary

The title complex (+)-**13x** has been prepared in an enantiomerically pure form. Its absolute configuration has been determined by single-crystal X-ray diffraction and has been correlated chemically to that of the 5,6-dimethylidene-2-norbornyl derivatives (−)-**1**, (−)-**2**, (−)-**3** and to (−)-(1*S*,2*R*)-benzonorborn-5-en-2-yl acetate (s. *Scheme 1*), whose configuration was deduced by indirect techniques. A critical analysis of the chiroptical properties of the exocyclic dienes **1**-**3** is now possible. These compounds are limiting systems for the application of the allylic axial chirality rule, the generalized octant rule and the symmetry rule for β,γ-unsaturated ketones.

Introduction. - The enantiomerically pure 5,6-dimethylidene-2-norbornyl derivatives **1**-**3** have been prepared for the first time by *Sonney & Vogel* [1]. Their chirality was deduced by chemical correlation with the (+)-benzonorborn-5-en-2-yl acetate whose (1*R*,2*S*)-configuration was based on three independent, indirect techniques [2].

Scheme 1[2])



(+)-**1** $\Delta\varepsilon_{248} = +0.33$

(+)-**2** $\Delta\varepsilon_{245} = +1.8$

(+)-**3** $\Delta\varepsilon_{248} = +10.3$[2])

---

[1]) Authors to whom correspondence should be addressed.

[2]) CD. spectra taken in isooctane.

0018-019X/81/7/2328-10$01.00/0

Very little is known about the chiroptical properties of exocyclic s-butadienes grafted onto rigid bicyclic skeletons [3] [4]. The 'allylic axial chirality rule' [5] led to contradictory predictions about the absolute configuration of **1**–**3** (and the acetates of **1** and **2**) when applied in analogy with (+)-2,3-dimethylidenebornane (**4**) and (–)-2-methylidenebornane (**5**) [3].

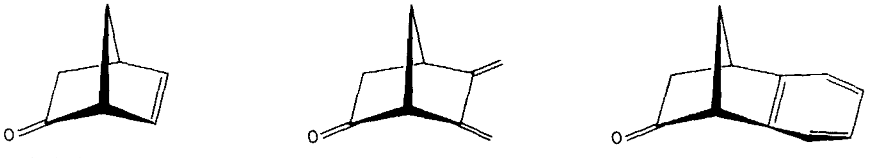
Scheme 2

(+)-**4** $\Delta\varepsilon_{250} = -0.6$

(–)-**5** $\Delta\varepsilon_{200} = -4.4$

An attempt to exploit the *Cotton* effect *(C. E.)* of the n→π* (CO) transition of (+)-**3** in order to confirm the configuration of these systems was also problematic. A weak negative *C. E.* was measured at 285 nm ($\Delta\varepsilon = -1.69$) in $CHCl_3$. In isooctane, an apparent double signal was observed in the CD. spectrum between 265 and 340 nm [1]. This showed that the chiroptical properties of the β,γ-unsaturated ketone **3** cannot be compared with those of related systems such as 2-norborn-5-enone **6** [6] and benzo-2-norborn-5-enone **7** [2].

Scheme 3



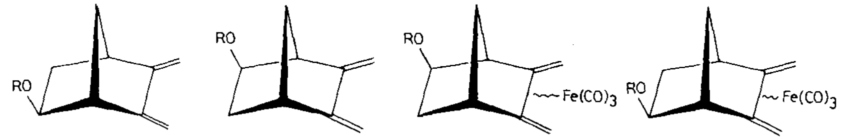
(+)-**6** $\Delta\varepsilon_{309} = +14.8$

(+)-**3** $\Delta\varepsilon_{288} = -1.2$ $\Delta\varepsilon_{318} = +0.59$

(+)-**7** $\Delta\varepsilon_{307.5} = +18.8^{2)}$

It became obvious that the absolute configuration of **1**–**3** had to be confirmed by a direct method before the striking CD. characteristics of these compounds could be discussed and a new theory could be developed. We chose to determine the absolute configuration of the (+)-5,6-dimethylidene-2*exo*-norbornyl-*exo*-irontricarbonyl *p*-bromobenzoate ((+)-**13x**) by single crystal X-ray crystallography. This structure also establishes the configuration of the irontricarbonyl complexes *(exo vs. endo)* of all the 5,6-dimethylidene-2-norbornyl derivatives, a task difficult to carry out unambiguously by the usual chemical and spectroscopic techniques [7].

Results. – Optical resolution was achieved by fractional crystallization of the camphanates (+)-**8** and (–)-**9** [1]. When stirred in MeOH with $Fe_2(CO)_9$ at 40°, (–)-**9** gave a mixture of the complexes (+)-**10x** (50%), (–)-**10n** (15%) and (+)-**12x** (30%). When heated in C_6H_6 with (benzalacetone)$Fe(CO)_3$ (70°, 72 h), *Scheme 4*



R = camphanyl: (+)-**8** (−)-**9** (+)-**10x** (−)-**11x**
(−)-**10n** (+)-**11n**
R = H (+)-**1** (−)-**1** (+)-**12x** (−)-**12x**
(−)-**12n** (+)-**12n**
R = p-Br-C_6H_4CO (+)-**13x** (−)-**13x**
x = *exo*-Fe$(CO)_3$
n = *endo*-Fe$(CO)_3$

pure (+)-**10x** could be obtained (55%). Methanolysis of (+)-**10x** (MeOH, K_2CO_3) gave the alcohol (+)-**12x** which was esterified into the parabromobenzoate (+)-**13x**. Similarly, (−)-**10n** gave (−)-**12n**. The enantiomers (−)-**12x**, (−)-**13x** and (+)-**12n** were derived from (−)-**11x** and (+)-**11n**, respectively. The analytical and spectroscopic data of all complexes are given in the experimental part. The assignment of the NMR. spectra was based on selective irradiations, lanthanide induced shifts and on the comparison of $\Delta\delta = \delta$(ligand) − δ(complex) with those of known (diene)Fe$(CO)_3$ complexes [7]. The configuration of all complexes could

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

Formula	(+)($BrC_{16}H_{15}O_2$)Fe$(CO)_3$	Radiation	Mo-K_α. Nb filtered (λ = 0.71069 Å)
Molecular mass	459.08	μ (cm^{-1})	30.4
Dimensions (mm)	0.10 × 0.14 × 0.26	Min. & max. transmission	0.678 and 0.761
Crystal system	Orthorhombic	Scan method	2θ-θ
Space group	$P2_12_12_1$	Background from	Scan profile interpretation [15]
a (Å)	7.271 (1)	$(\sin\theta/\lambda)_{max}$	0.54 Å^{-1}
b (Å)	13.072 (2)	Data collected	$+h, +k, +l$; $-h, -k, -l$
c (Å)	20.180 (2)	No. of unique reflections[a])	2946
V (Å^3)	1918.0 (7)	No. of reflections ($I < 3\sigma$)	1571
Z	4	No. of reflections/ No. of parameters	12.5
d_{obs} (g cm^{-3})	1.58 (1) (ZnI_2 solution)	Resolution method	*Patterson* and *Fourier*
d_{calc} (g cm^{-3})	1.59	Refinement method	Block-diagonal least-squares
F_{000}	920	Function minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Systematic extinctions	$h00: h = 2n+1$	w	$1/\sigma^2$
	$0k0: k = 2n+1$	R	0.039
	$00l: l = 2n+1$	R_w	0.028
		Goodness of fit	1.21

[a]) In point symmetry 222.

Table 2. *List of atomic parameters for complex (+)-(1S,2R)-***13x**.
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. These coordinates give the correct configuration of the molecule in a right hand coordinate system. The e.s.d. of the last significant digit is given in parentheses.

Atom	X	Y	Z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.5324 (1)	0.97784 (6)	0.55965 (5)	0.1042 (9)	0.0586 (5)	0.1161 (9)	−0.0041 (6)	0.0143 (7)	−0.0173 (6)
C(1)	0.452 (1)	0.3631 (6)	0.3720 (5)	0.062 (8)	0.050 (6)	0.061 (7)	0.021 (6)	−0.004 (6)	0.021 (5)
C(2)	0.459 (1)	0.3793 (5)	0.4464 (4)	0.065 (6)	0.052 (5)	0.043 (6)	−0.009 (5)	0.000 (6)	0.000 (5)
C(3)	0.602 (1)	0.2976 (5)	0.4670 (4)	0.061 (6)	0.061 (5)	0.047 (6)	−0.002 (5)	−0.011 (6)	0.010 (4)
C(4)	0.657 (1)	0.2461 (7)	0.4030 (4)	0.047 (7)	0.075 (7)	0.046 (6)	0.013 (6)	0.008 (5)	−0.008 (6)
C(5)	0.486 (1)	0.1873 (6)	0.3819 (4)	0.067 (8)	0.045 (5)	0.049 (6)	−0.001 (7)	0.002 (6)	0.000 (5)
C(6)	0.357 (1)	0.2617 (7)	0.3629 (4)	0.064 (8)	0.045 (6)	0.028 (5)	−0.013 (7)	−0.012 (5)	−0.007 (5)
C(7)	0.650 (1)	0.3375 (7)	0.3562 (3)	0.087 (8)	0.068 (6)	0.038 (6)	−0.043 (7)	−0.002 (5)	−0.009 (6)
C(8)	0.438 (1)	0.0850 (5)	0.3780 (3)	0.088 (8)	0.054 (5)	0.064 (6)	0.005 (6)	0.038 (6)	−0.003 (5)
C(9)	0.188 (1)	0.2332 (6)	0.3392 (4)	0.080 (7)	0.052 (6)	0.072 (7)	0.005 (6)	0.006 (6)	0.004 (5)
C(10)	0.492 (1)	0.5124 (5)	0.5212 (5)	0.056 (6)	0.030 (6)	0.078 (8)	0.009 (6)	−0.011 (7)	−0.008 (6)
C(11)	0.517 (1)	0.6248 (6)	0.5279 (4)	0.056 (6)	0.079 (7)	0.018 (5)	0.007 (6)	0.004 (5)	−0.006 (5)
C(12)	0.526 (1)	0.6914 (6)	0.4757 (3)	0.063 (6)	0.074 (6)	0.024 (5)	−0.012 (6)	0.007 (5)	−0.005 (5)
C(13)	0.535 (1)	0.7960 (6)	0.4849 (4)	0.088 (8)	0.039 (5)	0.056 (6)	−0.018 (6)	−0.010 (6)	0.008 (5)
C(14)	0.531 (1)	0.8349 (6)	0.5471 (5)	0.051 (6)	0.064 (6)	0.074 (7)	−0.007 (6)	−0.005 (6)	−0.021 (7)
C(15)	0.525 (1)	0.7712 (8)	0.6015 (4)	0.099 (8)	0.080 (7)	0.051 (7)	−0.022 (7)	0.000 (7)	−0.028 (6)
C(16)	0.515 (1)	0.6675 (7)	0.5900 (4)	0.072 (7)	0.056 (5)	0.060 (7)	−0.001 (7)	−0.012 (6)	0.018 (5)
C(17)	0.249 (1)	0.0634 (7)	0.2594 (5)	0.084 (9)	0.097 (9)	0.084 (8)	−0.002 (6)	−0.016 (7)	−0.038 (7)
C(18)	0.389 (2)	0.2493 (8)	0.2236 (4)	0.125 (9)	0.13 (1)	0.054 (9)	−0.021 (9)	−0.008 (8)	−0.004 (7)
C(19)	0.611 (2)	0.1164 (8)	0.2596 (5)	0.093 (9)	0.107 (8)	0.085 (8)	0.007 (7)	0.025 (8)	−0.006 (6)
Fe	0.3959 (2)	0.15862 (9)	0.28670 (6)	0.079 (1)	0.0764 (9)	0.0529 (8)	0.0010 (9)	0.0050 (9)	−0.0102 (9)
O(1)	0.5148 (7)	0.4834 (4)	0.4587 (3)	0.091 (4)	0.045 (3)	0.052 (4)	−0.002 (4)	0.009 (4)	−0.022 (3)
O(2)	0.4539 (8)	0.4565 (3)	0.5675 (3)	0.117 (5)	0.053 (4)	0.055 (4)	−0.010 (4)	−0.004 (4)	0.007 (3)
O(3)	0.1444 (9)	−0.0023 (5)	0.2448 (3)	0.096 (6)	0.120 (6)	0.145 (6)	−0.007 (5)	−0.003 (5)	−0.069 (5)
O(4)	0.388 (1)	0.3145 (5)	0.1840 (3)	0.189 (8)	0.139 (6)	0.082 (6)	−0.013 (7)	−0.018 (6)	0.030 (5)
O(5)	0.752 (1)	0.0844 (6)	0.2403 (4)	0.116 (7)	0.187 (8)	0.133 (7)	0.022 (6)	0.034 (6)	−0.037 (6)
H(1)	0.4003	0.4195	0.3470	0.0040					
H(2)	0.3440	0.3587	0.4679	0.0040					
H(3n)	0.5599	0.2503	0.4995	0.0040					
H(3x)	0.7089	0.3331	0.4873	0.0040					
H(4)	0.7689	0.2081	0.4038	0.0040					
H(7s)	0.7373	0.3901	0.3686	0.0040					
H(7a)	0.6749	0.3192	0.3112	0.0040					
H(8E)	0.5236	0.0319	0.3835	0.0040					
H(8Z)	0.3261	0.0629	0.4044	0.0040					
H(9E)	0.1103	0.2827	0.3190	0.0040					
H(9Z)	0.1119	0.1889	0.3660	0.0040					
H(12)	0.5410	0.6629	0.4319	0.0040					
H(13)	0.5345	0.8435	0.4476	0.0040					
H(15)	0.5332	0.7996	0.6459	0.0040					
H(16)	0.5050	0.6213	0.6272	0.0040					

be deduced from that of (+)-**13x** in the crystalline state, since no epimerization was observed upon dissolving the solids in chloroalkanes, even containing traces of protic acids.

Structure determination and absolute configuration of complex (+)-13x. - Single crystal diffraction intensities were collected on a Syntex $P2_1$ autodiffractometer. An absorption correction based on the *Gaussian* integration method was applied. *Table 1* gives crystallographic data and data collection procedure; the X-Ray 72 System of programs [8] was used. Atomic scattering factors for neutral Br, C, Fe and O [9] and anomalous dispersion coefficients for Br and Fe [10] were included in the structure factor calculations. The Br-atoms were located on the *Patterson* map and the remaining non-hydrogen atoms could be identified on successive *Fourier* maps. The calculated positions of the H-atoms were included in the structure factor but not refined.

The absolute configuration of the molecule was determined from a comparison of two separate refinements with opposite signs of the atomic positional parameters. The parameters of *Table 2* give the better agreement ($R = 0.039$; $R_w = 0.028$; GoF. = 1.21) compared with $R = 0.055$; $R_w = 0.053$ and GoF. = 2.18 for the inverse structure. On the basis of *Hamilton*'s test [11] the inverted structure can be rejected with a confidence level of more than 99.999%. The largest peaks in the final difference synthesis are about 1 $e^-/Å^3$ in the vicinity of the heavy atoms[3]).

Calculated bond lengths and angles are listed in *Tables 3* and *4*, respectively. Information about several least-squares planes and dihedral angles is presented in *Table 5*. A view of the molecular structure, prepared by the program ORTEP [12] is given in the *Figure*, 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 $(BrC_{16}H_{15}O_2)Fe(CO)_3$ molecules. All inter-

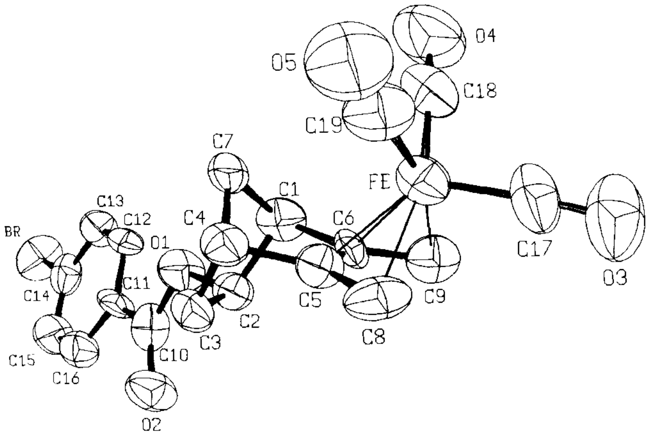


Figure. *A perspective view of the molecular structure of (+)-(1*S*, 2*R*)-5, 6-dimethylidene-2-*exo*-norbornyl-*exo*-irontricarbonyl* p-*bromobenzoate* ((+)-**13x**)

---

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

Table 3. *Bond lengths (Å) in (+)-***13x**.
The e.s.d. of the last significant digit is given in parentheses.

Fe–C(5)	2.063 (8)	C(5)–C(8)	1.38 (1)
Fe–C(6)	2.064 (8)	C(6)–C(9)	1.37 (1)
Fe–C(8)	2.102 (7)	C(10)–C(11)	1.49 (1)
Fe–C(9)	2.086 (9)	C(10)–O(1)	1.33 (1)
Fe–C(17)	1.73 (1)	C(10)–O(2)	1.22 (1)
Fe–C(18)	1.74 (1)	C(11)–C(12)	1.37 (1)
Fe–C(19)	1.74 (1)	C(11)–C(16)	1.37 (1)
C(1)–C(2)	1.52 (1)	C(12)–C(13)	1.38 (1)
C(1)–C(6)	1.51 (1)	C(13)–C(14)	1.35 (1)
C(1)–C(7)	1.51 (1)	C(14)–C(15)	1.38 (1)
C(2)–C(3)	1.55 (1)	C(14)–Br	1.886 (8)
C(2)–O(1)	1.441 (8)	C(15)–C(16)	1.38 (1)
C(3)–C(4)	1.51 (1)	C(17)–O(3)	1.18 (1)
C(4)–C(5)	1.52 (1)	C(18)–O(4)	1.17 (1)
C(4)–C(7)	1.52 (1)	C(19)–O(5)	1.18 (1)
C(5)–C(6)	1.40 (1)		

molecular contacts are equal to or greater than the sum of *van der Waals* radii. The $Fe(CO)_3$ group is in the *exo* position with respect to the roof-shaped ligand. The arrangement of ligands about the Fe-atom is tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints (a and b, *Table 5*) of the outer C,C-bonds of the diene system. The apex-to-base angles are 103° for the carbonyl groups and 111° for the C,C-bond midpoints. The basal angles are 92, 94 and 62°, 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.

Table 4. *Bond angles (°) in (+)-***13x**.
The e.s.d. of the last significant digit is given in parentheses.

C(5)–Fe–C(6)	39.7 (3)	C(1)–C(6)–C(5)	105.8 (8)
C(5)–Fe–C(8)	38.8 (3)	C(1)–C(6)–C(9)	133.9 (8)
C(6)–Fe–C(9)	38.5 (4)	C(5)–C(6)–C(9)	120.3 (8)
C(17)–Fe–C(18)	103.9 (5)	C(1)–C(7)–C(4)	94.2 (6)
C(17)–Fe–C(19)	103.0 (5)	C(11)–C(10)–O(1)	110.7 (7)
C(18)–Fe–C(19)	90.6 (5)	C(11)–C(10)–O(2)	123.5 (8)
C(2)–C(1)–C(6)	105.0 (7)	O(1)–C(10)–O(2)	125.9 (7)
C(2)–C(1)–C(7)	102.0 (7)	C(10)–C(11)–C(12)	124.3 (8)
C(6)–C(1)–C(7)	102.4 (7)	C(10)–C(11)–C(16)	118.9 (8)
C(1)–C(2)–C(3)	101.0 (6)	C(12)–C(11)–C(16)	116.5 (7)
C(1)–C(2)–O(1)	108.1 (6)	C(11)–C(12)–C(13)	121.8 (7)
C(3)–C(2)–O(1)	114.7 (6)	C(12)–C(13)–C(14)	119.7 (7)
C(2)–C(3)–C(4)	104.8 (6)	C(13)–C(14)–C(15)	120.8 (8)
C(3)–C(4)–C(5)	104.5 (7)	C(13)–C(14)–Br	119.8 (7)
C(3)–C(4)–C(7)	99.9 (7)	C(15)–C(14)–Br	119.5 (7)
C(5)–C(4)–C(7)	101.3 (7)	C(14)–C(15)–C(16)	117.6 (8)
C(4)–C(5)–C(6)	105.7 (7)	C(11)–C(16)–C(15)	123.6 (8)
C(4)–C(5)–C(8)	135.1 (8)	O(3)–C(17)–Fe	175.9 (8)
C(6)–C(5)–C(8)	111.2 (8)	O(4)–C(18)–Fe	175.9 (9)
		O(5)–C(19)–Fe	177.3 (9)

Table 5. *Least-squares planes in* (+)-**13x**

	Atoms defining plane	Equation of mean plane
Plane I	C(18), C(19), a, b	$4.834X+9.319Y+4.497Z=5.207$
Plane II	C(1), C(4), C(5), C(6), C(8), C(9)	$-2.576X+0.535Y+18.853Z=6.045$
Plane III	C(1), C(2), C(3), C(4)	$5.348X+8.716Y-2.421Z=4.682$
Plane IV	Br, C(10-16)	$7.260X-0.645Y+0.541Z=3.605$
Plane V	C(10), C(11), O(1), O(2)	$7.086X-1.850Y+3.510Z=4.364$
Plane VI	Fe, C(7), c, d, C(17), O(3)	$-4.817X+9.063Y-5.726Z=-2.116$

Displacement of atoms from mean plane (Å)

Plane I		Plane II		Plane III		Plane IV		Plane V		Plane VI	
C(18)	0.003	C(1)	−0.002	C(1)	0.001	Br	−0.068	C(10)	0.001	Fe	0.005
C(19)	−0.003	C(4)	−0.006	C(2)	−0.001	C(10)	−0.085	C(11)	0.000	C(7)	0.004
a	0.003	C(5)	0.003	C(3)	0.001	C(11)	0.034	O(1)	0.000	c	−0.003
b	−0.003	C(6)	0.016	C(4)	−0.001	C(12)	0.023	O(2)	−0.001	d	−0.010
Fe	−0.526	C(8)	−0.001			C(13)	0.029			C(17)	0.006
		C(9)	−0.010			C(14)	0.010			O(3)	−0.002
						C(15)	0.033				
						C(16)	0.024				

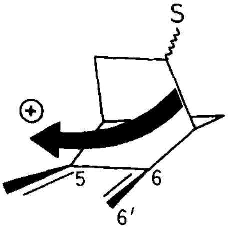
Dihedral angle between planes (°)

I-II 89.9; II-III 110.2; III-IV 45.7; IV-V 10.1; VI-I 89.5; VI-II 89.9; VI-III 89.5; VI-IV 45.3; VI-V 37.5
Normal to plane I/line Fe–C(17)–O(3) 4.6.

The geometrical features of the coordinated diene, as well as the coordination polyhedron, are quite comparable to those already discussed for analogous (exocyclic 1,3-diene)Fe$(CO)_3$ complexes [13] [14].

Conclusion. - The absolute configuration of (+)-(1*S*,2*R*)-5,6-dimethylidene-2-*exo*-norbornyl-*exo*-irontricarbonyl *p*-bromobenzoate ((+)-**13x**) proves unequivocally the absolute (1*R*,2*S*)-configuration of the exocyclic dienes (+)-**1**, (+)-**2** and (1*R*)-configuration of (+)-**3**. This work confirms also the absolute configuration of (+)-(1*R*,2*S*)-benzonorborn-5-en-2-yl acetate [2] which has been correlated chemically with (+)-**1** [1]. When applied to the exocyclic dienes (+)-**1**, (+)-**2** and (+)-**3**, the 'allylic axial chirality rule' must consider the C-atoms C(5,6) as π-system (positive *C.E.*, *cf.* [16]) instead of the methylidene function C(6,6′) as proposed by *Burgstahler et al.* [3] for the bornane derivatives (+)-**4** and (+)-**5**. The CD. spectrum of (+)-**3** is not understood yet. Further β,γ-unsaturated ketones with

Scheme 5



exocyclic s-*cis*-butadiene chromophores have to be prepared and investigated. Contrary to our observations [1], the new symmetry rule for β,γ-unsaturated ketones of *Shingu et al.* [17] predicts a positive *C.E.* near 300 nm for (+)-**3**. The chiroptical characteristics of the irontricarbonyl complexes are under study; they will be reported elsewhere.

We thank the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and the *'Fonds Herbette'* (Lausanne) for generous financial support.

Experimental Part

General Remarks. All reactions were carried out under Ar and the solvents were dried and degassed by standard methods [19]. Melting points (m.p.) (not corrected), *Tottoli* apparatus. IR. spectra ($\tilde{\nu}$[cm^{-1}]) in CCl_4, *Perkin-Elmer 577* spectrophotometer. Mass spectra (MS.) in electron ionization mode, HP 5980 GC-MS *Hewlett-Packard* spectrometer (*m/z* [amu] (% base peak), peaks corresponding to ^{56}Fe). ^{1}H-NMR. spectra, *Bruker WH 360* (360 MHz) and *WP 80* (80 MHz) spectrometers: δ[ppm], number of protons, tentative attribution [LIS.: relative shift induced by addition of Eu(dpm)$_3$]; apparent coupling constants *J*[Hz]. ^{13}C-NMR. spectra, *Bruker WH 360* (90.55 MHz) and *WP 60* (15.08 MHz) spectrometers (D signal of $CDCl_3$ as lock signal, δ_C of $CDCl_3$ as internal reference (76.91 ppm)): δ[ppm], apparent $^1J_{C,H}$ coupling constant (±1 Hz), tentative attribution; *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. Rotation angles $[\alpha]^{25}_{\lambda}$ in $CHCl_3$, *Perkin-Elmer 141* polarimeter. Abbreviations: *aq.* = aqueous, RT. = room temperature, sat. = saturated. Elementary analyses were performed by the *Mikrolabor* of the ETH, Zürich *(E. Manzer)*.

Preparation of complexes. – Preparation of (+)-**10x**, (–)-**11x**, (–)-**10n** *and* (+)-**11n**. A typical procedure is given for the isomer (+)-**10x**: a solution of (±)-**1** [1] (36,6 g) and camphanic acid chloride (74 g) in pyridine (300 ml) was stirred at RT. for 48 h. The solution was poured in ice/water, and the precipitate was filtered off and washed with water to eliminate [pyH]Cl. The crude camphanates (+)-**8** and (–)-**9** (75 g; yield 87%) was resolved by fractional crystallization from hexane. The diastereoisomer (–)-**9** crystallized as small cubes ($[\alpha]^{25}_{589} = -52°$). (+)-**8** was more soluble and crystallized as agglomerated needles ($[\alpha] = +27°$). (–)-**9** (5 g) and $Fe_2(CO)_9$ (6 g) were stirred in methanol (400 ml) at 40° for 24 h. After filtration and reduction to a small volume, the solution was chromatographed on a column (60×2 cm) packed with silica gel. Elution with hexane/ethyl acetate 4:1 brought down $Fe_3(CO)_{12}$, then three yellow fractions. Recrystallization from hexane/ether 1:1 at –25° gave (+)-**10x** (50%), (–)-**10n** (15%) and (+)-**12x** (30%). The same procedure starting with (+)-**8** gave (–)-**11x**, (+)-**11n** and (–)-**12x** in comparable yields. The following reaction gave exclusively the exo isomer (+)-**10x**. Compound (–)-**9** (5.8 g) and (benzalacetone)Fe(CO)$_3$ [18] (6.3 g) were heated in benzene (200 ml) at 70° for 72 h. Filtration followed by chromatography on silica gel (80×2 cm) using hexane/CH_2Cl_2 85:15 (*v/v*) as eluent gave complex (+)-**10x** (4.6 g, 55%) after recrystallization from hexane/ether 1:1 at –25°. The same reaction starting with (+)-**8** gave (–)-**11x** (56%). The direct reaction between the racemic alcohol (±)-**1** and $Fe_2(CO)_9$ followed by esterification of (±)-**12x** by camphanic acid chloride gave a mixture of diastereomers (+)-**10x** and (–)-**11x** that could not be resolved by fractional crystallization.

Data of (+)-**10x**. Yellow crystals, m.p. 156–157°, $[\alpha]^{25}_{589} = +30.5°$. – IR.: 2060, 1980, 1970 (CO), 1800, 1730 (COO). – MS. (70 eV): 456 (2, M^+), 428 (10, $M^+ - CO$), 400 (18, $M^+ - 2\,CO$), 372 (100, $M^+ - 3\,CO$).

$C_{22}H_{24}O_7Fe$ (456.28) Calc. C 57.89 H 5.26% Found C 57.98 H 5.28%

Data of (–)-**11x**. M.p. 151–152°, $[\alpha]^{25}_{589} = -34.9°$. – MS.: 456 (2), 428 (15), 400 (23), 372 (100).

Found C 58.01 H 5.35%

Data of (+)-**11n**. Yellow crystals, m.p. 163°, $[\alpha]^{25}_{589} = +70.8°$ – MS.: 456 (2), 428 (12), 400 (40), 372 (100). – IR.: 2060, 1980, 1960, 1795, 1732.

Found C 57.70 H 5.30%

Data of (–)-**10n**. M.p. 169°, $[\alpha]^{25}_{589} = -71.5°$. – MS.: 456 (2), 428 (4), 400 (36), 372 (100).

Found C 57.67 H 5.32%

Preparation of (+)-**12x**, (–)-**12x**, (+)-**12n**, (–)-**12n**. A typical procedure is given for (+)-**12x**: a solution of (+)-**10x** (4.6 g) and K_2CO_3 (8 g) in methanol (200 ml) was heated at 55° for 24 h. Removal of solvent, extraction with dichloromethane, and chromatography on silica gel (60×3 cm) using hexane/CH_2Cl_2 (9:1)→(5:5) gave complex (+)-**12x** (1.8 g, 65%) after recrystallization from hexane at –25°. The same reaction starting with (–)-**10n**, (–)-**11x** and (+)-**11n** gave (–)-**12n**, (–)-**12x** and (+)-**12n**, respectively.

Data of **12x**. Yellow crystals, m.p. 99–100°. For (+)-**12x**: $[\alpha]^{25}_{589} = +12.2°$; for (–)-**12x**: $[\alpha] = -12.4°$. – IR.: 2060, 1980, 1970 (CO), 3620 (OH). – ^{1}H-NMR. ($CDCl_3$ 25° [LIS.]): 4.33 (*m*, 1H, H(2) [100%]); 2.77 (*m*, 1H, H(4) [25%]); 2.67 (*m*, 1H, H(1) [59%]); 2.66 (*s*, OH); 2.17 (octuplet, 1H, H(3n) [42%]); 1.97 (*m*, 1H, H(7)$_{syn}$ [58%]); 1.87 (*d*, 2H, H(8,9)$_E$ [10%]); 1.79 (*m*, 1H, H(7)$_{anti}$ [28%]); 1.77 (*m*, 1H, H(3x) [70%]); 0.33 and 0.30 (2*d*, each 1H, H(8,9)$_Z$ [11%]); $J(1,2) < 1$, $J(1,7a) \simeq J(1,7s) \simeq J(4,7a) \simeq J(4,7s) \simeq 1.5$, $J(2,3x) < 3$, $J(2,3n) = 6.2$, $J(2,7a) = 2.5$, $J(3x,3n) = 12.5$, $J(3x,4) = 3.6$, $J(3n,7a) = 2.5$, $J(7a,7s) = 9.5$ and $J(E,Z) = 2.3$. – ^{13}C-NMR. ($CDCl_3$): 210.8 (*s*, CO); 113.1 and 107.3 (2*s*, C(5,6)); 72.8 (*d*, 153, C(2)); 49.2 (*d*, 152, C(1)); 41.2 (*t*, 135, C(3)); 39.9 (*d*, 140, C(4)); 38.6 (*t*, 140, C(7)); 33.6 and 33.3 (2*t*, 160, C(8,9)). – MS.: 276 (13, M^+), 248 (48, M^+ – CO), 220 (76, M^+ – 2 CO), 192 (95, M^+ – 3 CO), 174 (61), 148 (95), 91 (95), 56 (100).

$C_{12}H_{12}O_4Fe$ (276.08) Calc. C 52.21 H 4.38% Found C 52.29 H 4.49%

Data of **12n**. Yellow crystals, m.p. 90–91°. For (+)-**12n**: $[\alpha]^{25}_{589} = +38.8°$; for (–)-**12n**: $[\alpha] = -38.8°$. – IR.: 2060, 1980, 1960 (CO), 3620 (OH). – ^{1}H-NMR. (80 MHz, $CDCl_3$ 25° [LIS.]): 4.52 (*m*, 1H, H(2) [100%]); 2.95 (*m*, 1H, H(1) [65%]); 2.82 (*m*, 1H, H(4) [27%]); 2.07 (*m*, 1H, H(7)$_{syn}$ [74%]); 1.95 and 1.77 (2*d*, each 1H, H(8,9)$_E$ [12] and [16%], respectively); 1.82 and 1.81 (2*m*, 2H, H(7)$_{anti}$ [40%] and H(3n) [47%]); 1.78 (*m*, 1H, H(3x) [84%]); 0.47 and 0.32 (2*d*, each 1H, H(8,9)$_Z$ [13%]); $J(E,Z) = 2.4$, for other *J*'s, see **12x**. – ^{13}C-NMR. (15.08 MHz, $CDCl_3$): 211.1 (*s*, CO); 123.6 and 115.6 (2*s*, C(5,6)); 75.8 (*d*, 153, C(2)); 51.8 (*t*, 137, C(3)); 50.1 (*d*, 146, C(1)); 44.7 (*t*, 133, C(7)); 42.6 (*d*, 148, C(4)); 35.2 and 33.3 (2*t*, 160, C(8,9)). – MS.: 276 (5), 248 (35), 220 (70), 192 (68), 174 (50), 172 (35), 148 (100), 91 (40), 56 (60).

$C_{12}H_{12}O_4Fe$ (276.08) Calc. C 52.21 H 4.38% Found C 52.68 H 4.49%

Preparation of (+)- *and* (–)-**13x**. A solution of (+)-**12x** (0.3 g) and *p*-BrC_6H_4COCl (0.26 g) in pyridine (10 ml) was stirred at 0° for 24 h. The solution was poured in ice/water, extracted with chloroform, and the combined extracts washed successively with 5% HCl-solution, sat. aq. $NaHCO_3$-solution and water. After drying over $MgSO_4$, chromatography on *Florisil* and recrystallization from hexane gave complex (+)-**13x** (0.4 g, 80%). Starting with (–)-**12x** gave the isomer (–)-**13x** (80%). Single crystals for the X-ray analysis were grown by slow cooling of a solution of (+)-**13x** in hexane to –20°.

Data of (+)-**13x**. Yellow crystals, m.p. 118–120°, $[\alpha]^{25}_{589} = +16.4°$. – IR.: 2060, 1980, 1970 (CO), 1720 (COO). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.93 and 7.61 (2*d*, each 2H, $J(H,H) = 8.5$); 5.33 (*m*, 1H, H(2)); 2.99 (*m*, 1H, H(1)); 2.85 (*m*, 1H, H(4)); 2.34 (*m*, 1H, H(3n)); 2.04 (*m*, 1H, H(3x)); 1.97 and 1.92 (2*d*, each 1H, H(8,9)$_E$); 1.94 (*m*, H(7)$_{syn}$); 1.87 (*m*, 1H, H(7)$_{anti}$); 0.42 and 0.40 (2*d*, each 1H, H(8,9)$_Z$); $J(1,2) \simeq J(4,3n) < 1$, $J(1,7s) \simeq J(1,7a) \simeq J(4,7s) \simeq J(4,7a) \simeq 1.5$, $J(2,3x) = 3.0$, $J(2,3n) = 6.5$, $J(2,7a) \simeq J(3n,7a) \simeq 2.5$, $J(3x,3n) = 13.0$, $J(3x,4) = 3.5$, $J(7a,7s) = 9.0$, $J(E,Z) = 2.1$. – ^{13}C-NMR. (90.55 MHz, $CDCl_3$): 210.7 (*s*, CO); 165.3 (*s*, C=O); 131.6 and 130.9 (2*d*, 164, C(12,13,15,16)); 128.9 and 128.0 (2*s*, C(11,14)); 113.6 and 106.5 (2*s*, C(5,6)); 75.8 (*d*, 158, C(2)); 46.6 (*d*, 149, C(1)); 42.3 (*t*, 143, C(3)); 40.1 (*d*, 145, C(4)); 36.7 (*t*, 137, C(7)); 34.4 and 33.9 (2*t*, 161, C(8,9)). – MS. (^{81}Br – ^{79}Br): 460–458 (3–4, M^+), 432–430 (14–18, M^+ – CO), 404–402 (26–33, M^+ – 2 CO), 376–374 (40–63, M^+ – 3 CO), 222 (44), 91 (100).

$C_{19}H_{15}BrO_5Fe$ (459.08) Calc. C 49.71 H 3.29% Found C 49.80 H 3.27%

Data of (–)-**13x**. $[\alpha]^{25}_{589} = -16.8°$.

Found C 49.86 H 3.21%

REFERENCES

[1] *J.-M. Sonney & P. Vogel,* Helv. Chim. Acta *63,* 1034 (1980).

[2] *D.D. Sandman, K. Mislow, W.P. Giddings, J. Dirlam & G.C. Hanson,* J. Am. Chem. Soc. *90,* 4877 (1968).

[3] *A. W. Burgstahler, D.L. Boger & N.C. Naik,* Tetrahedron *32,* 309 (1976).

[4] *F. Dallacker, M. Erkens & S. Kusumawati,* Chem. Ber. *111,* 3191 (1978).

[5] *A.W. Burgstahler, R.C. Barkhurst & J.K. Gawronski,* in 'Modern Methods of Steroid Analysis', E. Heftmann, Ed., Academic Press, New York 1973, Chap. 16, cf. also: *E. Charney, C.-H. Lee & J.S. Rosenfield,* J. Am. Chem. Soc. *101,* 6802 (1979).

[6] *K. Mislow & J.G. Berger,* J. Am. Chem. Soc. *84,* 1956 (1962); *K. Mislow,* Ann. New York Acad. Sci. *93,* 459 (1962).

[7] *U. Steiner, H.-J. Hansen, K. Bachmann & W. von Philipsborn,* Helv. Chim. Acta *60,* 643 (1977).

[8] *J.M. Stewart, F.A. Kundell & J.C. Baldwin,* X-ray 72, version of June 1972, Technical Report TR-192 of the Computing Science Center, University of Maryland (as modified by *D. Schwarzenbach*).

[9] *D.T. Cromer & J.B. Mann,* Acta Cryst. A *24,* 321 (1968).

[10] *D.T. Cromer,* Acta Cryst. *18,* 17 (1965).

[11] *S.C. Abrahams & S. Ramaseshan,* 'Anomalous Scattering', Munskgaard, Copenhagen 1975, p. 314.

[12] *C.K. Johnson,* ORNL-3794, Oak Ridge National Laboratory 1971.

[13] *A.A. Pinkerton, G. Chapuis, P. Vogel, U. Hänisch, Ph. Narbel, T. Boschi & R. Roulet,* Inorg. Chim. Acta *35,* 197 (1979).

[14] *J. Wenger, Nguyen H. Thuy, T. Boschi, R. Roulet, A. Chollet, P. Vogel, A.A. Pinkerton & D. Schwarzenbach,* J. Organometal. Chem. *174,* 89 (1979).

[15] *H. Blessing, P. Coppens & P. Becker,* J. Appl. Cryst. *7,* 488 (1972); *D. Schwarzenbach,* 'TWOTHLEH', a Syntex $P2_1$ data collection program including scan profile interpretation, Abs. Fourth European Crystallographic Meeting, 1977, p. 134.

[16] *J. Gawronski & K. Gawronska,* J. Chem. Soc., Chem. Commun. *1980,* 346.

[17] *H. Kuritani, K. Shingu & M. Nakagawa,* Tetrahedron Lett. *1980,* 529.

[18] *J.A.S. Howell, B.F.G. Johnson, P.L. Josty & J. Lewis,* J. Organometal. Chem. *39,* 329 (1972).

[19] *D.D. Perrin, W.L.F. Armarego & D.R. Perrin,* 'Purification of Laboratory Chemicals', Pergamon, London, 1966; D.F. Shriver, 'The Manipulation of Air-sensitive Compounds', McGraw Hill, New York 1969.