

**82. Condensation of 2,3-Di(methylidene)-7-oxabicyclo[2.2.1]heptane Derivatives into Dicarbonyl[ $\eta^3:\eta^3$ -octa-2,6-diene-1,8-diyl]iron Complexes with Nonacarbonyliron. Crystal Structure of (1*RS*,2*RS*,3*RS*,4*SR*,5*RS*,6*SR*,1'*RS*,2'*RS*,3'*RS*,4'*SR*,5'*RS*,6'*SR*)-Dicarbonyl- $\{(2,3, C-\eta:2',3', C-\eta)$ -2,2'-ethylene-5,5',6,6'-tetrakis(methanesulfonyloxy)-methyl]-3,3'-di(methylidene)-bis[7-oxabicyclo[2.2.1]hept-2-yl]}iron**

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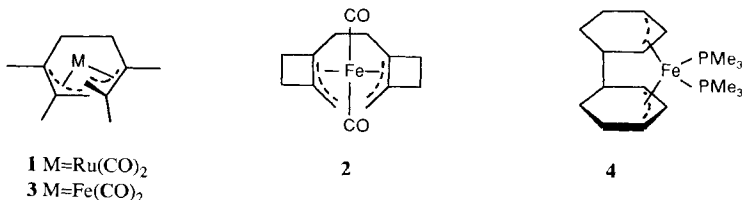
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The reactions of  $[\text{Fe}_2(\text{CO})_9]$  with 2-*exo*,3-*exo*-bis(chloromethyl)-5,6-di(methylidene)-7-oxabicyclo[2.2.1]-heptane (**5**) and with 5,6-di(methylidene)-7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dimethyl bis(methanesulfonate) (**6**) afforded, together with the corresponding [*exo*- $\text{Fe}(\text{CO})_3(1,3\text{-diene})$ ] complexes **7** and **8**, the products of dimerization in the form of stable  $[\text{Fe}(\text{CO})_2\{(1,2,3-\eta:6,7,8-\eta)\text{-octa-2,6-diene-1,8-diyl}\}]$  complexes **9** and **10**, respectively, with high stereoselectivity. The structure of **10** was established by means of single-crystal X-ray diffraction.

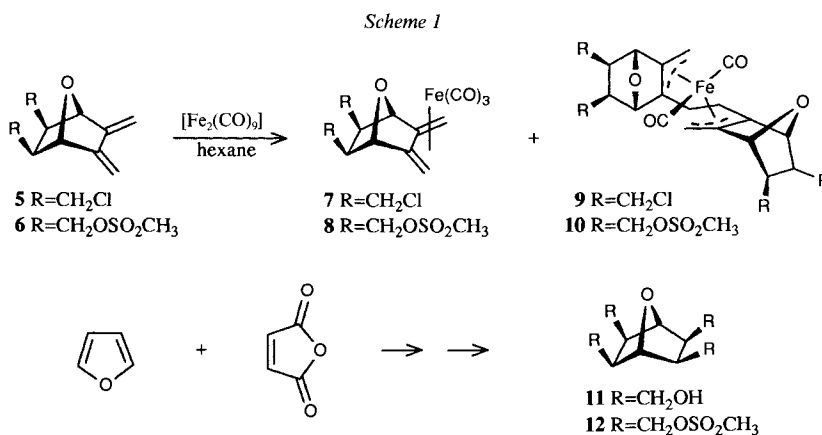
**Introduction.** – The oligomerization of 1,3-dienes with catalysts containing low-valent transition-metal complexes is thought to involve, in many instances, the intermediacy of  $[(1,2,3-\eta:6,7,8-\eta)\text{-octa-1,6-diene-1,8-diyl}]\text{metal}$  complexes [1] [2]. Evidences for such species have been obtained, *e.g.*, by NMR studies of Ni-catalyzed 1,3-diene cyclo-dimerization [3] [4] and by the X-ray crystal structure of dicarbonyl $[(1,2,3-\eta:6,7,8-\eta)$ -2,3,6,7-tetramethyloctadienediyl]ruthenium (**1**) obtained by carbonylation of carbonyl(2,3-dimethylbutadiene)<sub>2</sub>ruthenium [5]. Although the parent  $[\text{Fe}(\eta^3\text{-alkyl})_2(\text{CO})_2]$  complex has been described already in 1967 by *Nesmeyanov* and coworkers [6], very few examples of related derivatives have been reported since then [7–9]. *King* and *Harmon* [10] found the first case of dicarbonyl(octadienediyl)iron complex. On heating 1,2-di(methylidene)cyclobutane with  $\text{Fe}_3(\text{CO})_{12}$  in benzene, complex **2** was obtained in low yield.



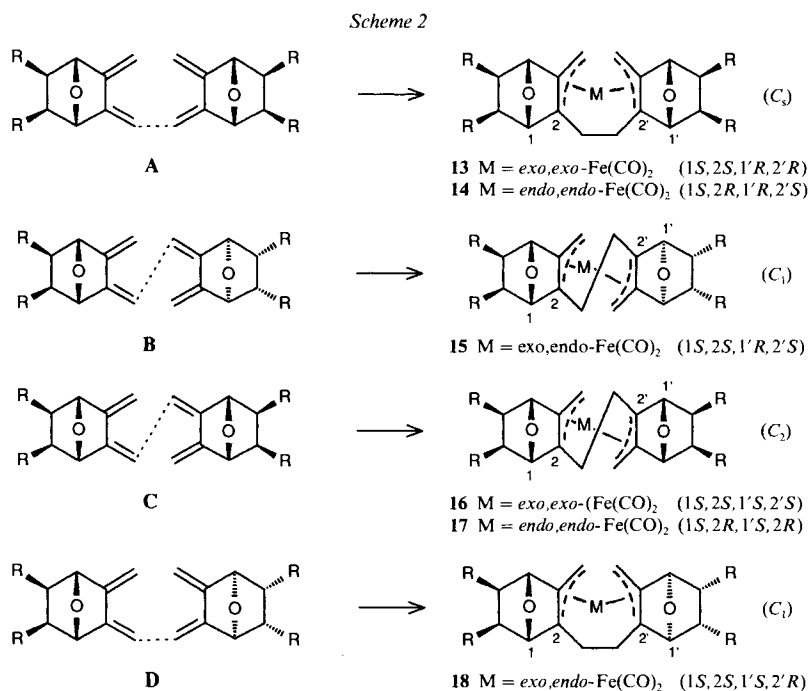
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Cox *et al.* [5] reported that carbonylation of carbonyl(2,3-dimethylbutadiene)<sub>2</sub>iron in THF gives the corresponding bis(allyl) complex **3** in 19% yield together with tricarbonyl-(2,3-dimethylbutadiene)iron. Structures of the iron complexes **2** and **3** were deduced from their spectral data. The related iron complex **4** was prepared on treating cyclohexa-1,3-diene with (benzene)bis(trimethylphosphine)iron, and its crystal structure has been reported recently by Green *et al.* [11]. In continuation of our exploration of the reactivity of carbonyliron complexes toward *s-cis*-butadiene systems grafted onto bicyclic skeletons [12] [13], we have found that dienes **5** and **6** react with [Fe<sub>2</sub>(CO)<sub>9</sub>] to give, together with the expected [Fe(CO)<sub>3</sub>(η<sup>4</sup>-diene)] complexes **7** and **8**, the corresponding of [Febis(allyl)(CO)<sub>2</sub>] derivatives **9** and **10**, respectively. Crystal and molecular structure of **10** has been determined by X-ray diffraction analysis. It is shown that the 1,3-diene dimerization process is highly *exo*-face selective with respect to the 7-oxabicyclo[2.2.1]heptane skeleton.

**Results and Discussion.** – Diene **5** was derived from the *Diels-Alder* adduct of furan and maleic anhydride *via* tetrol **11** following a procedure developed earlier in our laboratory [14] (*Scheme 1*). On stirring **5** in hexane with an excess of [Fe<sub>2</sub>(CO)<sub>9</sub>] at 20° for several days, a mixture was obtained from which the known [Fe(CO)<sub>3</sub>(diene)] complex **7** [15] (72–79%) and the new [Febis(allyl)(CO)<sub>2</sub>] complex **9** (4–8%) could be isolated by column chromatography on silica gel. The elemental analysis of **9** confirmed a formula [Fe(CO)<sub>2</sub>(**5**)<sub>2</sub>], and the 360-MHz <sup>1</sup>H-NMR spectrum showed two *m* at 0.90 and 1.53 ppm (*AA'XX'* pattern), characteristic of a CH<sub>2</sub>CH<sub>2</sub> moiety maintaining either the C<sub>s</sub> or the C<sub>2</sub> symmetry, and two *s* at 2.65 and 3.67 ppm, typical of the protons of the methyldiene groups coordinated to the Fe(CO)<sub>2</sub> moiety [5] [10]. The <sup>13</sup>C-NMR spectrum of **9** displayed typical signals at 38.6, 92.89, and 110.6 ppm for the Fe(η<sup>3</sup>-alkyl)<sub>2</sub> moiety. These spectral data, however, did not allow one to establish the relative configuration of the metallic group (*exo* vs. *endo* with respect to the 7-oxabicyclo[2.2.1]heptane skeleton); they permitted, however, to exclude the C<sub>1</sub> structures like **15** and **18** (see below, *Scheme 2*), thus ruling out the mode **B** and **D** of dimerization. No distinction could be made between the *meso*-compounds of type **13** or **14** (C<sub>s</sub> symmetry) and racemic mixtures of systems like **16** and **17** (C<sub>2</sub> symmetry). Since no good monocrystal of **9** could be obtained for X-ray diffraction studies, we prepared the diester analogue **10** in the following way.



Quadruple esterification of tetrol **11** with  $\text{MeSO}_2\text{Cl}$ /pyridine gave the tetramesylate **12** whose treatment with 4.4 equiv. of *t*-BuOK in DMF (20°, 72 h) gave diene **6** in 91% yield. Stirring **6** with an excess of  $[\text{Fe}_2(\text{CO})_9]$  in degassed benzene (20°, 3–4 d) led to a mixture from which complexes **8** (74%) and **10** (4–6%) could be isolated by column chromatography on silica gel. A single crystal of formula  $(\mathbf{10})_2 \cdot \text{CH}_2\text{Cl}_2$  was obtained by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . X-Ray diffraction studies (see below) demonstrated that **10** was formed according to mode C and has the *exo,exo* relative configuration of the metallic moiety (see **6**, Scheme 2). The spectral data of **8** and **10** were very similar to those of **7** and **9**, respectively. The *exo* relative configuration of the  $\text{Fe}(\text{CO})_3$  moieties in **7** and **8** was indicated by the observation of long-range coupling constants (0.5–0.7 Hz) between the bridgehead and methylenide protons [12a] [15].



The formation of dicarbonyl( $\eta^3:\eta^3$ -octa-2,6-diene-1,8-diyl)iron complexes on treatment of 1,3-dienes with  $[\text{Fe}_2(\text{CO})_9]$  has never been reported, except for the related experience of King and Harmon [10] in which  $[\text{Fe}_3(\text{CO})_{12}]$  in benzene was employed with 1,2-di(methylenide)cyclobutane. The yields obtained for the bis(allylic) complexes **9** and **10** are quite modest at this moment. Experiments are planned to evaluate the importance of structural parameters of the diene, solvent, concentration, and the presence of acid catalysts on the outcome of the dimerization process and on the stereoselectivity of the formation of the corresponding bis(allyl)dicarbonyliron complexes.

**Crystal Structure Determination of  $(\mathbf{10})_2 \cdot \text{CH}_2\text{Cl}_2$ .** – Complex **10** was first recrystallized from MeCN/MeOH and then from anhydrous  $\text{CH}_2\text{Cl}_2$ . This gave relatively large,

Table 1. Crystal Data of  $C_{26.5}H_{37}ClFeO_{16}S_4 \cdot (10)_2 \cdot CH_2Cl_2$ 

Crystal Data			
Formula	$C_{26.5}H_{37}ClFeO_{16}S_4$	$\beta$ [°]	80.85(2)
Crystal system	triclinic	$\gamma$ [°]	79.07(2)
Space group	$P\bar{1}$	$V$ [Å <sup>3</sup> ]	1679.1(8)
Temp. [K]	110	$Z$	2
$a$ [Å]	8.038(2)	$\mu$ (MoK $\alpha$ ) [cm <sup>-1</sup> ]	8.37
$b$ [Å]	14.703(2)	$D_{calc}$ [gcm <sup>-3</sup> ]	1.63
$c$ [Å]	15.387(2)	Molecular weight [amu]	831.225
$\alpha$ [°]	71.02(2)		
Parameters and Results Pertinent to the Data Collection			
Diffractometer	Syntex R3m	$2\theta$ range	0 to 60°
Diffraction geometry	equatorial	$\sin(\theta/\lambda)_{max}$	0.701
Radiation	MoK $\alpha$ , graphite mono-chromatized ( $\lambda = 0.71069$ Å)	Number of variables	585
Scan width	$((K\alpha_1 + 1) - (K\alpha_2 + 1))^{\circ}$	Number of reflexions per variables	17
Scan speed	4 to 15 deg · min <sup>-1</sup>	Final agreement factors	$R_F = 0.033$
Scan type	$2\theta:\omega$		$R_w = 0.036$
Background	stationary		$G \circ F = 2.99$
Reflections collected	$\pm h \pm k \pm l$		maximal shift/e.s.d.
	10493 unique reflections,		0.05 (scale factor)
	of which 8833 observed		average shift/e.s.d.
Observation criterion	$I(h) > 3$ e.s.d. ( $I(h)$ )		0.032
Agreement between equivalent reflections	$R_{int} = 0.0234$		

pale yellow slabs. The measured crystal (Table 1) was bounded by a natural (100) pinacoid, natural (010), (110), (117), (401), (011), and (013) pedions and a (171) fracture plane. This latter plane was created when the crystal was mechanically reduced to a suitable size. An absorption correction based on the morphology described above did improve only slightly the agreement factor between equivalent intensities. Three periodically monitored check reflections indicated that the crystal did not decay to any detectable degree during the data collection.

The structure was solved by means of a combination of direct, Patterson and Fourier methods [16]. The 85 atoms were refined (using anisotropic displacement parameters for non-H-atoms and isotropic for H-atoms) in three blocks to a final  $R_F$  value of 0.033. The quantity refined was  $\Sigma w\Delta F$ ; the weight,  $w$ , was set to the inverse of the estimated standard deviation of  $F$ . All parameters converged nicely, except for the displacement parameter of atom H(32) which was negative; it was set invariant and equal to a value similar to other H-atoms.

The residues found in the cavity built out of the methanesulfonate and the carbonyl groups can satisfactorily be explained as a Cl- and half a C-atom (see Fig. 1). These atoms may be interpreted as a disordered molecule of  $CH_2Cl_2$ . The residual electron density (three peaks over  $1 \text{ e}\text{\AA}^{-3}$ ) could, unfortunately, not be woven into a convincing model of disorder. The hypothesis of a disordered solvent molecule inside the cavity is, however, quite appealing and certainly compatible with the data.

A difference map at  $R_F = 0.033$  revealed three maxima between 2.3 and  $1.0 \text{ e}\text{\AA}^{-3}$ . These residues as well as most of the 25 next strongest maxima were near the Cl- or C-atoms. Otherwise they lay off the rest of the molecules and did not suggest any further molecular fragment.

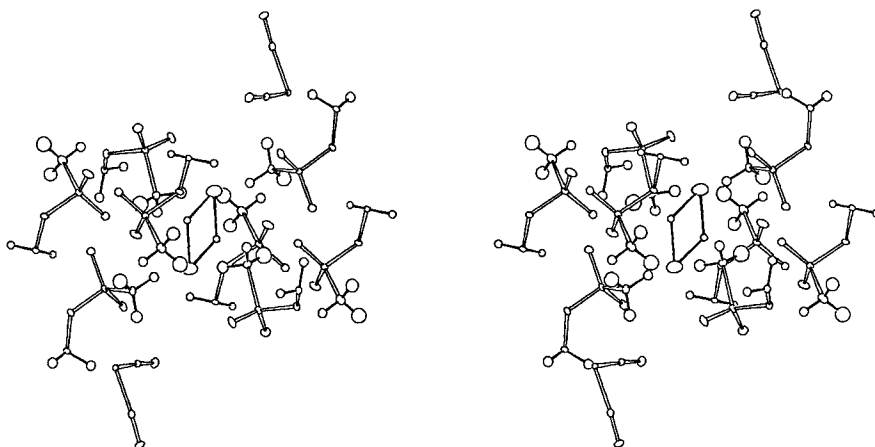


Fig. 1. Stereoscopic representation of the cavity built out of eight methanesulfonate and two carbonyl groups of  $(10)_2CH_2Cl_2$ . Inside, a disordered molecule of  $CH_2Cl_2$  (mother liquor) is represented.

Atomic coordinates, tables of observed and calculated structure factors, anisotropic displacement factors, and a detailed description of data collection, structure solution, and refinement are available as supplementary material from the authors upon request and are deposited with the *Cambridge Crystallographic Data Center*. Bond lengths and angles, interatomic distances, and selected torsion angles are given in *Tables 2–4*. The  $C_2$  symmetry of complex **10** is visible in *Fig. 2*. The same local symmetry was also found in complexes **1** [5], **4** [11], and in (cyclooctatetraene)zirconium [8c]. The projection of part of **10** along an axis going through the bridgehead centers of the bicyclic systems (*Fig. 3*) shows

Table 2. Selected Bond Distances [Å]<sup>a)</sup>

Fe–C(11)	1.779(1)	C(26)–C(27)	1.423(2)	C(61)–O(61)	1.472(2)
Fe–C(12)	1.780(2)	C(26)–C(44)	1.528(2)	C(71)–O(71)	1.473(2)
Fe–C(21)	2.132(2)	C(27)–C(28)	1.404(2)	C(81)–O(81)	1.470(2)
Fe–C(22)	2.067(2)	C(27)–C(41)	1.520(2)	S(1)–C(52)	1.748(2)
Fe–C(23)	2.203(1)	C(31)–O(31)	1.440(2)	S(1)–O(51)	1.568(1)
Fe–C(26)	2.186(2)	C(31)–C(32)	1.559(2)	S(1)–O(52)	1.427(1)
Fe–C(27)	2.066(2)	C(32)–C(33)	1.571(2)	S(1)–O(53)	1.431(4)
Fe–C(28)	2.129(2)	C(32)–C(51)	1.516(3)	S(2)–C(62)	1.751(2)
Cl–C(1)	1.616(4)	C(33)–C(34)	1.540(2)	S(2)–O(61)	1.575(1)
Cl–C(1) <sup>b)</sup>	1.809(4)	C(33)–C(61)	1.524(2)	S(2)–O(62)	1.428(1)
C(11)–O(11)	1.155(2)	C(34)–O(31)	1.436(2)	S(2)–O(63)	1.421(2)
C(12)–O(12)	1.149(2)	C(41)–O(41)	1.437(2)	S(3)–C(72)	1.747(2)
C(21)–C(22)	1.404(2)	C(41)–C(42)	1.556(3)	S(3)–O(71)	1.579(1)
C(22)–C(23)	1.416(2)	C(42)–C(43)	1.565(2)	S(3)–O(72)	1.432(1)
C(22)–C(31)	1.522(3)	C(42)–C(81)	1.513(2)	S(3)–O(73)	1.431(1)
C(23)–C(24)	1.500(3)	C(43)–C(44)	1.554(2)	S(4)–C(82)	1.755(2)
C(23)–C(34)	1.529(2)	C(43)–C(71)	1.516(2)	S(4)–O(81)	1.573(1)
C(24)–C(25)	1.513(2)	C(44)–O(41)	1.444(2)	S(4)–O(82)	1.428(1)
C(25)–C(26)	1.503(2)	C(51)–O(51)	1.479(2)	S(4)–O(83)	1.427(2)

<sup>a)</sup> Numbers in parentheses are estimated standard deviations in the last significant digit.

<sup>b)</sup>  $1 - x, \bar{y}, 1 - z$ .

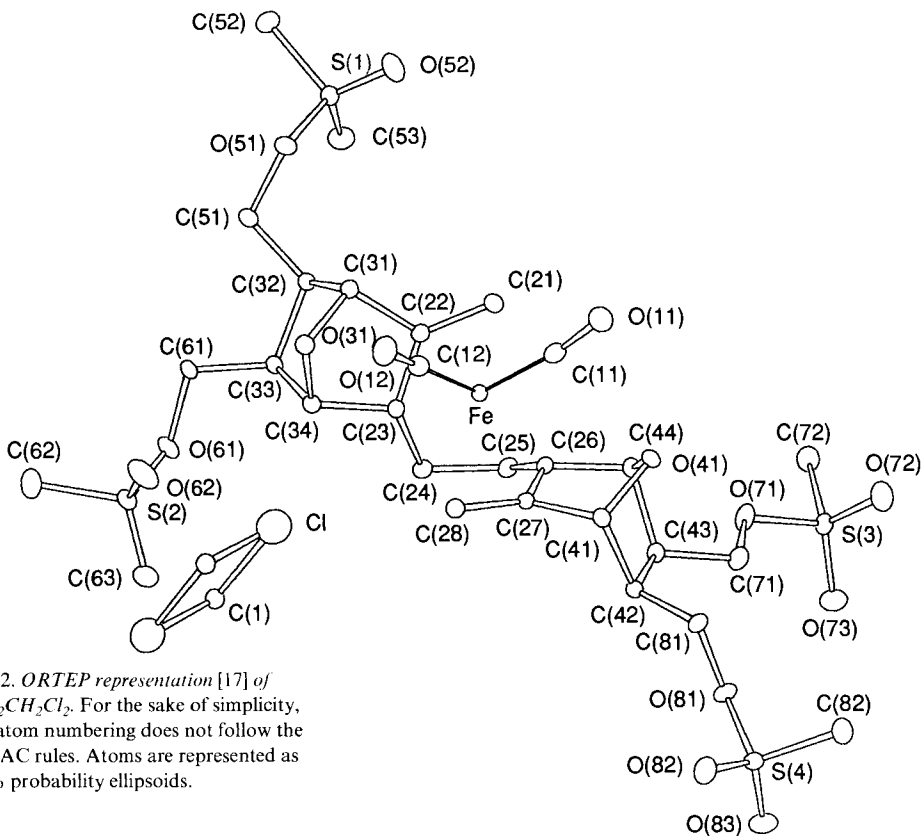


Fig. 2. ORTEP representation [17] of  $(10)_2CH_2Cl_2$ . For the sake of simplicity, the atom numbering does not follow the IUPAC rules. Atoms are represented as 50% probability ellipsoids.

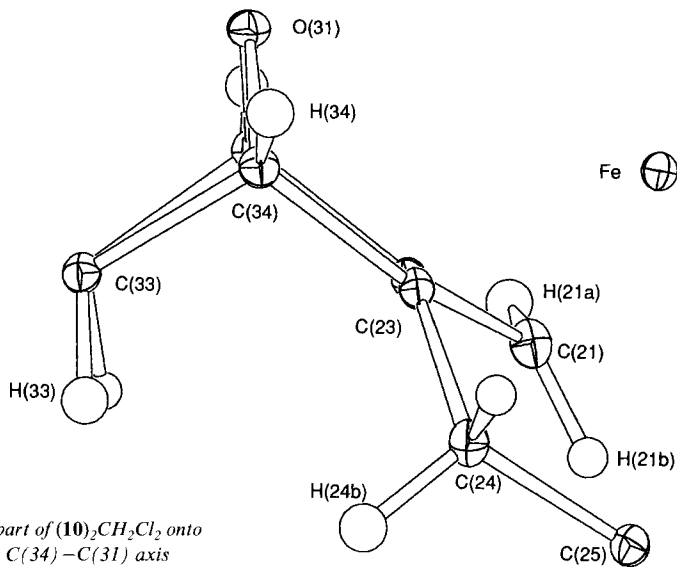


Fig. 3. Projection of part of  $(10)_2CH_2Cl_2$  onto a plane normal to the  $C(34)-C(31)$  axis

Table 3. Selected Bond Angles [°]<sup>a)</sup>

C(11)–Fe–C(12)	88.19(8)	C(41)–O(41)–C(44)	95.4(1)
Fe–C(11)–O(11)	172.6(2)	C(41)–C(42)–C(43)	100.3(1)
Fe–C(12)–O(12)	173.1(1)	C(42)–C(43)–C(44)	100.7(1)
C(21)–C(22)–C(23)	129.8(2)	C(43)–C(44)–O(41)	101.3(1)
C(21)–C(22)–C(31)	125.3(1)	C(43)–C(44)–C(26)	107.0(1)
C(22)–C(23)–C(34)	103.0(1)	C(51)–O(51)–S(1)	120.3(1)
C(23)–C(24)–C(25)	111.0(1)	C(61)–O(61)–S(2)	120.7(1)
C(24)–C(25)–C(26)	111.1(1)	C(71)–O(71)–S(3)	115.7(1)
C(25)–C(26)–C(27)	131.6(1)	C(81)–O(81)–S(4)	118.5(1)
C(25)–C(26)–C(44)	116.9(1)	C(51)–S(1)–C(52)	103.0(1)
C(26)–C(27)–C(28)	129.6(1)	O(51)–S(1)–O(52)	105.95(7)
C(26)–C(27)–C(41)	104.4(1)	O(51)–S(1)–O(53)	109.40(7)
C(28)–C(27)–C(41)	125.2(1)	O(61)–S(2)–C(62)	104.23(8)
C(22)–C(31)–O(31)	103.9(1)	O(61)–S(2)–O(62)	109.26(6)
C(22)–C(31)–C(32)	103.7(1)	O(61)–S(2)–O(63)	104.90(8)
C(31)–O(31)–C(34)	96.2(1)	O(71)–S(3)–C(72)	98.47(8)
C(31)–C(32)–C(33)	100.6(1)	O(71)–S(3)–O(72)	109.55(8)
C(32)–C(33)–C(34)	100.3(1)	O(71)–S(3)–O(73)	108.83(7)
C(33)–C(34)–C(23)	107.7(1)	O(81)–S(4)–C(82)	104.27(7)
C(33)–C(34)–O(31)	100.5(1)	O(81)–S(4)–O(82)	110.02(8)
C(27)–C(41)–C(42)	106.1(1)	O(81)–S(4)–O(83)	104.16(7)
C(27)–C(41)–O(41)	104.5(1)	C1–C(1)–C(1)–C1 <sup>b)</sup>	119.4(2)

<sup>a)</sup> Numbers in parentheses are estimated standard deviations in the last significant digit.

<sup>b)</sup>  $1 - x, \bar{y}, 1 - z$ .

Table 4. Selected Torsion Angles [°]<sup>a)</sup>

C(52)–S(1)–O(51)–C(51)	102.8(1)	S(3)–O(71)–C(71)–C(43)	–172.8(1)
O(52)–S(1)–O(51)–C(51)	–142.5(1)	O(71)–C(71)–C(43)–C(42)	–177.7(1)
O(53)–S(1)–O(51)–C(51)	–13.3(1)	O(71)–C(71)–C(43)–C(44)	–64.1(1)
S(1)–O(51)–C(51)–C(32)	83.0(1)	C(82)–S(4)–O(81)–C(81)	–74.7(1)
O(51)–C(51)–C(32)–C(33)	167.6(1)	O(82)–S(4)–O(81)–C(81)	41.5(1)
O(51)–C(51)–C(32)–C(31)	52.7(1)	O(83)–S(4)–O(81)–C(81)	170.5(1)
C(62)–S(2)–O(61)–C(61)	91.2(1)	S(4)–O(81)–C(81)–C(42)	–146.4(1)
O(62)–S(2)–O(61)–C(61)	–25.1(1)	O(81)–C(81)–C(42)–C(41)	176.4(1)
O(63)–S(2)–O(61)–C(61)	–154.3(1)	O(81)–C(81)–C(42)–C(43)	–70.4(1)
S(1)–O(61)–C(61)–C(33)	–48.6(1)	C(21)–C(22)–C(23)–C(24)	–42.6(1)
O(61)–C(61)–C(33)–C(32)	171.8(1)	C(22)–C(23)–C(24)–C(25)	40.0(1)
O(61)–C(61)–C(33)–C(34)	–75.3(1)	C(23)–C(24)–C(25)–C(26)	48.7(1)
C(72)–S(3)–O(71)–C(71)	–172.7(1)	C(24)–C(25)–C(26)–C(27)	36.7(1)
O(72)–S(3)–O(71)–C(71)	–57.3(1)	C(24)–C(25)–C(26)–C(27)	36.7(1)
O(73)–S(3)–O(71)–C(71)	72.2(1)	C(25)–C(26)–C(27)–C(28)	–43.1(1)

<sup>a)</sup> Numbers in parentheses are estimated standard deviations in the last significant digit.

that the allylic moiety does not share the C(34)–C(23)–C(22)–C(31) average plane of the bicyclic skeleton; the methyldene moiety attached to the Fe-atom lies above that plane (toward the *exo*-face), the bond C(22)=CH<sub>2</sub>(21) (see Fig. 2) subtending an angle  $\alpha = 6^\circ$  with the average C(34)–C(23)–C(22)–C(31) plane. The methyldene moiety CH<sub>2</sub>(24) spans an angle  $\beta = 25^\circ$  with the average plane C(34)–C(23)–C(22)–C(31). The corresponding angles  $\alpha$  and  $\beta$  for the second part of the complex are 6 and 24°, respectively.

## Experimental Part

General. See [18].

**Reaction of 2-exo,3-exo-Bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane (5) with Nonacarbonyldiiron.** A mixture of **5** [14] [15] (1.06 g, 4.84 mmol) and  $[\text{Fe}_2(\text{CO})_9]$  (5.46 g, 15 mmol) in hexane (100 ml) was stirred at r.t. for 87 h. The mixture was filtered through *Celite*, and the filtrate was purified by column chromatography (CC; silica gel, petroleum ether/ $\text{CH}_2\text{Cl}_2$  gradient). After  $[\text{Fe}(\text{CO})_5]$  and  $[\text{Fe}_3(\text{CO})_{12}]$  were eluted with petroleum ether, two yellow bands were separated. From the first band, yellow crystals of *exo-tricarbonyl-[(C,5,6,C- $\eta$ )-2-exo,3-exo-bis(chloromethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane]iron* [15] (**7**); 1.32 g, 76% was obtained, and the second one gave yellow crystals **9** (60 mg, 4.5%).

(1RS,2RS,3RS,4SR,5SR,6RS,1'RS,2'RS,3'RS,4'SR,5'RS,5'SR,6'RS)-Dicarbonyl{(2,3,C- $\eta$ :2',3',C- $\eta$ )-5,5',6,6'-tetrakis(chloromethyl)-2,2'-ethylene-3,3'-(dimethylidene)bis[7-oxabicyclo[2.2.1]hept-2-yl]}iron (**9**). M.p. 190° (dec. without melting; MeCN). UV (MeCN): 236 (18700), 280 (sh, 5900), 351 (1600). IR (KBr): 1988, 1925, 1287, 1015, 918, 837, 775, 726, 673, 610.  $^1\text{H-NMR}$  (360 MHz,  $\text{CDCl}_3$ ): 0.90 (AA' of AA'XX', 2 H,  $\text{CH}_2$ ); 1.53 (XX' of AA'XX', 2 H,  $\text{CH}_2$ ); 2.44 (m, 2 H,  $\text{CHCH}_2\text{Cl}$ ); 2.65 (m, 2 H,  $\text{CHCH}_2\text{Cl}$ ); 2.65 (s, 2 H, C=CH); 3.47 (m, 4 H,  $\text{CH}_2\text{Cl}$ ); 3.67 (s, 2 H, C=CH); 3.70 (m, 4 H,  $\text{CH}_2\text{Cl}$ ); 4.20 (s, 2 H, OCH); 4.45 (s, 2 H, OCH).  $^{13}\text{C-NMR}$  (90.55 MHz,  $\text{CDCl}_3$ ): 22.2 ( $\text{CH}_2$ ); 38.6 (=CH<sub>2</sub>); 43.2 ( $\text{CH}_2\text{Cl}$ ); 43.5 ( $\text{CH}_2\text{Cl}$ ); 45.8 ( $\text{CHCH}_2\text{Cl}$ ); 48.6 ( $\text{CHCH}_2\text{Cl}$ ); 85.7 (OCH); 87.3 (OCH); 92.8 (C); 110.6 (C); 213.4 (CO). MS (70 eV): 548 (0.6,  $M^+$ ); 496 (1.0), 494 (1.4), 492 (1.4,  $[M - 2\text{CO}]^+$ ); 403 (1.8), 401 (1.5), 3.66 (1.3), 353 (4.7), 351 (7.7), 314 (7.1), 312 (11), 277 (7.5), 235 (7.1), 233 (7.0), 185 (11), 183 (14), 181 (11), 171 (14), 169 (12), 167 (10), 165 (12), 160 (15), 155 (15), 147 (17), 141 (20), 131 (20), 129 (28), 128 (26), 120 (23), 119 (38), 117 (29), 115 (34), 105 (32), 91 (100), 77 (61), 65 (48), 53 (69). Anal. calc. for  $\text{C}_{22}\text{H}_{24}\text{Cl}_4\text{FeO}_4$  (550.09): C 48.04, H 4.40; found: C 48.20, H 4.52.

**7-Oxabicyclo[2.2.1]heptane-2-exo,3-exo,5-exo,6-exo-tetramethyl Tetrakis(methanesulfonate) (12).** Methanesulfonyl chloride (19.7 ml, 250 mmol) was added dropwise to a stirred soln. of 7-oxabicyclo[2.2.1]heptane-2-exo,3-exo,5-exo,6-exo-tetramethanol [19] (5.45 g, 25 mmol) in anhyd. pyridine (110 ml) maintained at 0–5°. After stirring at 20° for 15 h, the mixture was poured into  $\text{H}_2\text{O}$  (1 l). The precipitate was washed with  $\text{H}_2\text{O}$  and dried *in vacuo* ( $\text{P}_4\text{O}_{10}$ ): 11.8 g (89%). Colourless crystals. M.p. 193.5–194.5° (dec.; MeCN). UV (MeCN): 214 (90). IR (KBr): 3200, 1330, 1163, 1008, 943, 820.  $^1\text{H-NMR}$  (80 MHz,  $(\text{D}_7)\text{DMF}$ ): 2.58 (m, 4 H, H–C(2), H–C(3), H–C(5), H–C(6)); 3.33 (s, 4  $\text{MeSO}_3$ ); 4.40 (m, 4  $\text{CH}_2\text{O}$ ); 4.50 (s, H–C(1), H–C(4)). Anal. calc. for  $\text{C}_{14}\text{H}_{26}\text{O}_{13}\text{S}_4$  (530.59): C 31.69, H 4.94; found: C 31.86, H 4.88.

**5,6-Di(methylidene)-7-oxabicyclo[2.2.1]heptane-2-exo,3-exo-dimethyl Bis(methanesulfonate) (6).** *t*-BuOK (4.93 g, 44 mmol) was added portionwise to a stirred soln. of **12** (10.6 g, 20 mmol) in anhyd. DMF (200 ml) at 20°. After stirring at 20° for 72 h, the mixture was poured into  $\text{H}_2\text{O}$  (900 ml) and the precipitate washed with  $\text{H}_2\text{O}$  and dried *in vacuo* ( $\text{P}_4\text{O}_{10}$ ): 5.1 g (76%) of **6**. A second crop of crystals was obtained in the following way. The filtrate obtained above was diluted with 1 l of  $\text{H}_2\text{O}$  and extracted with  $\text{CH}_2\text{Cl}_2$  (0.5 l, 3 times). The combined extracts were dried ( $\text{MgSO}_4$ ) and evaporated. The residue was recrystallized from  $\text{H}_2\text{O}$ : 1.1 g (16%) of **6**; total, 6.2 g (91%) of colourless crystals. M.p. 142–143° (dec., MeOH). UV (MeCN): 240 (8600). IR (KBr): 3014, 1355, 1343, 1164, 983, 946, 889, 868, 843, 822, 770.  $^1\text{H-NMR}$  (80 MHz,  $\text{CDCl}_3$ ): 2.58 (m, H–C(2), H–C(3)); 3.10 (s, 2  $\text{MeSO}_3$ ); 4.31 (m, 2  $\text{CH}_2\text{O}$ ); 4.81 (s, H–C(1), H–C(2)); 5.13, 5.38 (2s,  $\text{CH}_2=\text{C}(5)$ ,  $\text{CH}_2=\text{C}(6)$ ).  $^{13}\text{C-NMR}$  (90.55 MHz,  $\text{CDCl}_3$ ): 37.6 ( $\text{MeSO}_3$ ); 45.3 (C(2), C(3)); 67.3 ( $\text{CH}_2\text{O}$ ); 83.1 (C(1), C(4)); 102.9 ( $\text{CH}_2=\text{C}$ ); 145.8 (C(5), C(6)). Anal. calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_7\text{S}_2$  (338.39): C 42.59, H 5.36; found: C 42.69, H 5.40.

**Reaction of 6 with Nonacarbonyldiiron.** A mixture of **6** (3.0 g, 8.88 mmol) and  $[\text{Fe}_2(\text{CO})_9]$  (10.9 g, 30 mmol) in benzene (200 ml) was stirred at 20° for 67 h. The mixture was filtered through *Celite* and the filtrate purified by CC (silica gel). After  $[\text{Fe}(\text{CO})_5]$  and  $[\text{Fe}_3(\text{CO})_{12}]$  were eluted with petroleum ether, **8** was obtained with  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  1:1 to give 315 g (74%) of yellow crystals. Complex **10** was eluted with AcOEt to give 159 mg (4.5%) of yellow crystals.

(1RS,2SR,3RS,4SR,5RS,6SR)-Tricarbonyl[(C,5,6,C- $\eta$ )-5,6-di(methylidene)-7-oxabicyclo[2.2.1]heptane-2-exo,3-exo-dimethyl Bis(methanesulfonate)]iron (**8**). M.p. 164.5–166.0° (EtOH). UV (MeCN): 287 (4400). IR (KBr): 2050, 1962, 1946, 1367, 1327, 1174, 1162, 985, 953, 613.  $^1\text{H-NMR}$  (360 MHz,  $\text{CDCl}_3$ ): 0.41 (d,  $J = 2.5$ , 2 H, C=CH<sub>2</sub>); 2.11 (d,  $J = 2.5$ , 2 H, C=CH<sub>2</sub>); 3.25 (m, H–C(2), H–C(3)); 3.13 (s, 2 OMs); 4.35 (m, 2 H,  $\text{CH}_2\text{OMs}$ ); 4.50 (m, 2 H,  $\text{CH}_2\text{OMs}$ ); 4.74 (s, 2 H, OCH).  $^{13}\text{C-NMR}$  (90.55 MHz,  $\text{CDCl}_3$ ): 33.0 (C=CH<sub>2</sub>); 37.7 (OMs); 43.1 (CH); 67.8 ( $\text{CH}_2\text{OMs}$ ); 80.0 (OCH); 106.5 (C=CH<sub>2</sub>); 210.1 (CO). MS (70 eV): 422 (0.4,  $[M - 2\text{CO}]^+$ ), 315 (2), 285 (9), 248 (4), 230 (11), 220 (7), 162 (11), 151 (20), 147 (11), 135 (12), 133 (17), 119 (28), 118 (15), 117 (32), 115 (17), 105 (53), 95 (18), 94 (30), 92 (21), 91 (100), 84 (67), 83 (22), 81 (27), 79 (73), 77 (54), 67 (20), 65 (42), 57 (22), 56 (52), 55 (29), 53 (33), 51 (26), 43 (35), 41 (58), 40 (21). Anal. calc. for  $\text{C}_{15}\text{H}_{18}\text{FeO}_{10}\text{S}_2$  (478.27): C 37.67, H 3.79; found: C 37.73, H 3.87.



(1RS,2RS,3RS,4SR,5RS,6SR,1'RS,2'RS,3'RS,4'SR,5'RS,6'SR)-Dicarbonyl{(2,3-C- $\eta$ :2',3'-C- $\eta$ )-2,2'-ethylene 5,5',6,6'-tetrakis[(methanesulfonyloxy)methyl]-3,3'-di(methylidene)-bis[7-oxabicyclo[2.2.1]hept-1-yl]}-iron (10). M.p. ca. 150° (dec. without melting; MeCN/MeOH). UV (MeCN): 236 (17700), 277 (sh, 6000), 350 (1300). IR (KBr): 1987, 1928, 1348, 1168, 945, 810, 610. <sup>1</sup>H-NMR (360 MHz, CD<sub>3</sub>CN): 0.90 (AA' of AA'XX', 2 H, CH<sub>2</sub>); 1.53 (XX' of AA'XX', 2 H, CH<sub>2</sub>); 2.54 (m, 2 H, CHCH<sub>2</sub>OMs); 2.71 (m, 2 H, CHCH<sub>2</sub>OMs); 2.74 (d, J = 1.7, 2 H, C=CH); 3.05, 3.10 (2s, 4 MsO); 3.65 (d, J = 1.7, 2 H, C=CH); 4.16 (s, 2 H, OCH); 4.19, 4.35 (2m, 4 CH<sub>2</sub>OMs); 4.39 (s, 2 H, OCH). <sup>13</sup>C-NMR (90.55 MHz, CD<sub>3</sub>CN): 22.6 (CH<sub>2</sub>); 37.4 (OMs); 37.5 (OMs); 39.2 (=CH<sub>2</sub>); 42.0 (CHCH<sub>2</sub>OMs); 44.9 (CHCH<sub>2</sub>OMs); 69.8 (CH<sub>2</sub>OMs); 70.1 (CH<sub>2</sub>OMs); 85.0 (OCH); 86.5 (OCH); 94.8 (C); 111.8 (C); 215.3 (CO). Anal. calc. for C<sub>26</sub>H<sub>36</sub>FeO<sub>16</sub>S<sub>4</sub> (788.65): C 39.60, H 4.60; found: C 39.70, H 4.51. For a sample recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, anal. calc. for C<sub>26.5</sub>H<sub>37</sub>ClFeO<sub>16</sub>S<sub>4</sub> (831.225): C 38.29, H 4.49, Fe 6.73, S 15.43; found: C 37.91, H 4.33, Fe 6.64, S 15.68.

## REFERENCES

- [1] B. Barnett, B. Büssemeier, P. Heimbach, P. W. Jolly, C. Krüger, J. Tkatchenko, G. Wilke, *Tetrahedron Lett.* **1972**, 1457.
- [2] W. Keim, A. Behr, M. Röper, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, Chapt. 52.3
- [3] H. J. Kablitz, G. Wilke, *J. Organomet. Chem.* **1973**, *51*, 241; R. Baker, *Chem. Rev.* **1973**, *73*, 487.
- [4] R. Benn, B. Büssemeier, S. Holle, P. W. Jolly, R. Mynott, I. Tkatchenko, G. Wilke, *J. Organomet. Chem.* **1985**, *279*, 63.
- [5] D. N. Cox, R. Roulet, G. Chapuis, *Organometallics* **1985**, *4*, 2001; see also: D. N. Cox, R. Roulet, *J. Organomet. Chem.* **1988**, *342*, 87.
- [6] A. N. Nesmeyanov, I. I. Kritskaya, *J. Organomet. Chem.* **1968**, *14*, 387; A. N. Nesmeyanov, I. I. Kitskaya, Yu. A. Ustynuk, E. I. Fedin, *Dokl. Akad. Nauk SSSR* **1967**, *176*, 341.
- [7] M. Franck-Neumann, M. P. Heitz, D. Martina, A. de Cian, *Tetrahedron Lett.* **1983**, *24*, 1611.
- [8] a) J. M. Grosselin, P. H. Dixneuf, *J. Organomet. Chem.* **1986**, *314*, C76; see also: b) G. Huttner, V. Bejnenke, *Chem. Ber.* **1974**, *107*, 156; c) D. J. Brauer, C. Krüger, *Organometallics* **1982**, *1*, 207; d) J. Blümel, F. H. Köhler, G. Müller, *J. Am. Chem. Soc.* **1988**, *110*, 4846.
- [9] J. Chen, G. Lei, M. Shao, X. Xu, Z. Zhang, *J. Chem. Soc., Chem. Commun.* **1988**, 1296.
- [10] R. R. King, C. A. Harmon, *J. Am. Chem. Soc.* **1976**, *98*, 2409.
- [11] M. L. H. Green, D. O. Hare, L.-L. Wong, *J. Chem. Soc., Dalton Trans.* **1987**, 2031.
- [12] a) Ph. Vioget, M. Bonivento, R. Roulet, P. Vogel, *Helv. Chim. Acta* **1984**, *67*, 1638; b) E. Bonfantini, J.-L. Métral, P. Vogel, *ibid.* **1987**, *70*, 1791; S. Araki, E. Bonfantini, P. Vogel, *ibid.* **1988**, *71*, 1354; E. Bonfantini, P. Vogel, A. A. Pinkerton, *ibid.* **1989**, *72*, 906; c) F. Claret, P. Vogel, *Organometallics* **1990**, *9*, 2785.
- [13] P. Vogel, R. Roulet, in 'Organometallics in Organic Synthesis', Eds. H. Werner and G. Erker, Springer-Verlag, Berlin, 1989, Vol. II, p. 79.
- [14] C. Mahaim, P. Vogel, *Helv. Chim. Acta* **1982**, *65*, 866.
- [15] E. Meier, O. Cherpillod, T. Boschi, R. Roulet, P. Vogel, C. Mahaim, A. A. Pinkerton, D. Schwarzenbach, G. Chapuis, *J. Organomet. Chem.* **1980**, *186*, 247.
- [16] J. M. Stewart, F. A. Kundell, J. C. Baldwin, 'The XRAY72 System. Tech. Rep. TR-192', Computer Science Center, Univ. of Maryland, 1972, College Park, Maryland, USA.
- [17] C. K. Johnson, 'ORTEP. Report ORNL-3794', Oak Ridge National Laboratory, 1965, Tennessee.
- [18] J. Wagner, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1988**, *71*, 624.
- [19] C. Mahaim, P. A. Carrupt, J. P. Hagenbuch, A. Florey, P. Vogel, *Helv. Chim. Acta* **1980**, *63*, 1149.