88. Topospecific Reactions of a [5.5.5.5]Fenestradiene with $[Fe_2(CO)_9]$

by **Jing Wang**[a])[1]), **Régine Guidetti-Grept**[a])[2]), **Reinhart Keese**[a])*, and **Helen Stoeckli-Evans**[b])

[a]) Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern
[b]) Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel

(24.I.97)

N,N-Dimethylformamide dimethyl acetal transforms an allylic OH group, which is part of a tetracyclic hydrocarbon in a unique elimination reaction into a [5.5.5.5]fenestradiene (**2b** → **4**). In topologically selective reactions of this diene **4** with $[Fe_2(CO)_9]$, the $[Fe(CO)_4(\eta^2\text{-diene})]$ and the $(Fe(CO)_3(\eta^4\text{-diene})]$ complexes **8** and **9**, respectively, are formed by complexation on one side of the diene moiety, whereas complexation on the other side leads to a $[Fe(CO)_2(Cp)]$ complex **10**.

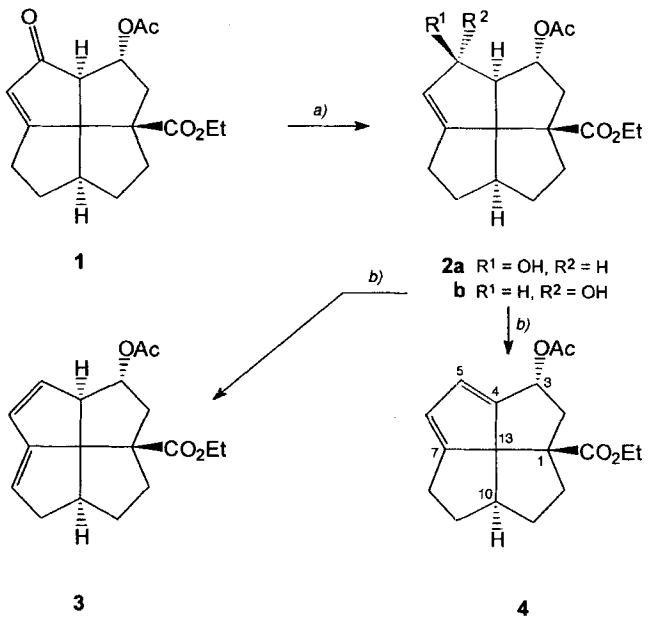
Introduction. – According to computational results, opposite bond angles at the central C-atom of [5.5.5.5]fenestranes (= dodecahydropentaleno[1,6-*cd*]pentalenes) can primarily be enlarged by inversion at the bridgeheads with the result of formation of *trans*-bicyclo[3.3.0]octane substructures or by introduction of bridgehead double bonds [1]. With efficient synthetic methods for functionalized [5.5.5.5]fenestranes in hand [2–4], we pursued the preparation of stereoisomeric [5.5.5.5]fenestranes by sigmatropic rearrangements[3]). In such compounds, the opening of the opposite bond angles in the central $C(C)_4$ moiety can further be enhanced by introduction of bridgehead double bonds. Since our early attempts to prepare a fenestradiene containing a cyclopentadiene moiety by a base-induced elimination reaction have been unsuccessful [6], we considered other methods for preparation. Here, we report a short and unusual elimination reaction by which a [5.5.5.5]fenestradiene containing a cyclopentadiene unit has been obtained as well as its reaction with $[Fe_2(CO)_9]$.

Results and Discussion. – In our recent study of the structural prerequisites for efficient sigmatropic rearrangements, we prepared the acetoxy alcohols **2a** and **2b** in a 1:1.3 ratio from the known enone **2** [2] by reduction with $NaBH_4/CeCl_3$ and treated both stereoisomers with *N,N*-dimethylformamide dimethyl acetal in refluxing xylene [7] [8]. Instead of reacting by [2,3]sigmatropic rearrangements, **2a** underwent a 1,4-elimination to the diene **3** (21%), whereas **2b** gave much to our surprise the diene **4** *via* 1,2-*syn*-

[1]) Postdoctoral fellow 1994–1996.
[2]) Part of the Ph.D. thesis, 1991–1994; present address: *Novartis AG*, Basel.
[3]) The direct formation of a saturated *cis,trans,cis,cis*-[5.5.5.5]fenestrane has been reported by *Wender* and coworkers [5].

elimination in an isolated yield of 46%. This lack of sigmatropic rearrangement in the case of **2a** and **2b** is in contrast to the successful *Claisen*-type [3,3]sigmatropic rearrangements at the α- as well as at the β-face of [4.5.5.5]fenestranes [11]. To the best of our knowledge, this mode of reaction of allylic alcohols with an *N,N*-dimethylformamide diacetal has not been described[4]). Contrary to our expectations, which was based on the failure to isolate such a diene in a structurally related case [6c], the diene **4**, being the first example of a fenestradiene with a cyclopentadiene substructure, proved to be rather stable under the high-temperature conditions used for its preparation.

Scheme 1

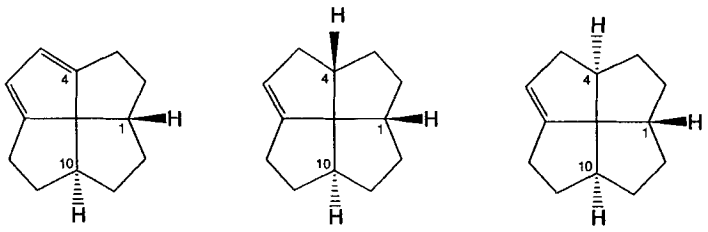


a) $NaBH_4/CeCl_3 \cdot 7\ H_2O$, MeOH, r.t. *b*) $Me_2NCH(OMe)_2$, xylene, reflux.

The topology of the cyclopentadiene unit of **4** is rather unique: On the β-face, '*syn*' to the ethoxycarbonyl group, the bridgehead double bond C(4)=C(5) is hyperstable, whereas the other one is highly strained with these relationships being reversed on the α-side [10] [12]. This is supported by AM1 [13] calculations for the unsubstituted tetracyclic hydrocarbons **5**–**7**: the strain increases by 25 kJ/mol when **6** is compared with **5**, whereas the release of strain is *ca.* 125 kJ/mol when the same bridgehead double bond C(4)=C(5) would be hydrogenated on the α-face[5]).

[4]) *V. Helbling*, recent CA and SCI search.

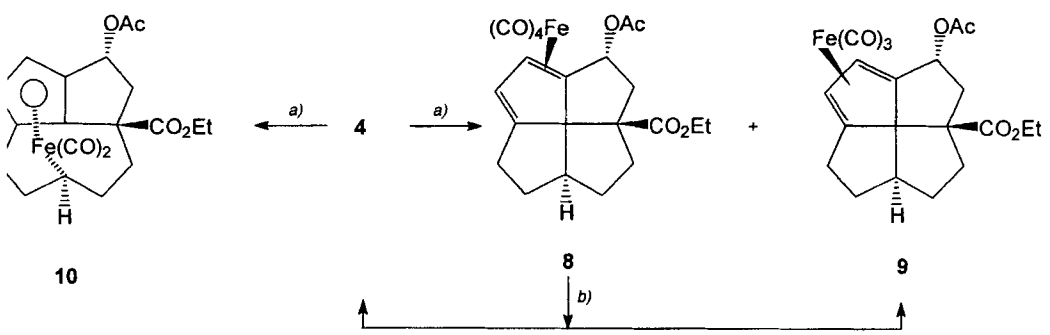
[5]) The strain energy (kJ/mol), *i.e.* ΔH_f°(AM1) $-\sum$ average bond energies, is estimated by using the *Laidler* increments [9] and a value of 20 kJ/mol for the π-delocalization of the diene in **5**. OS (olefinic strain) [10] for the formal transformation of **5** → **6** is −24.2, and for **5** → **7** + 121.1 kJ/mol. ΔH_f°(AM1) in kJ/mol: **5**, 135.5; **6**, 95.5; **7**, −50.2 ΔH_f° and strain energy of **7** are −50.1 and 4.6 kJ/mol; the values for **7** given in Table 3 of [1] are incorrect.



5 **6** **7**

For the introduction of further C=C bonds, we intended to stabilize the diene moiety in **4** by complexation with an appropriate transition-metal compound [14] [15]. When **4** was treated with $[Fe_2(CO)_9]$ at room temperature, the three ironcarbonyl complexes **8**–**10** were isolated (*Scheme 2*). The structures of **8** and **9** were established by means of their spectral data and their transformations. The $[Fe(CO)_4(\eta^2\text{-diene})]$ complex **8** is much more stable at $-70°$ and slowly reacted at room temperature to the $[Fe(CO)_3(\eta^4\text{-diene})]$ complex **9** and **4** in a 1.8:1 ratio; **10** could not be detected under these conditions. We interpret this transformation together with the high-field shift of the H–C(3) signal in the ^{1}H-NMR spectrum as evidence for complexation of the diene π-system with $Fe(CO)_4$ on the β-face.

Scheme 2



a) $[Fe_2(CO)_9]$, C_6H_6, r.t. *b*) (D_8)Toluene, $-70° \rightarrow$ r.t., 26d.

The structure of the $[Fe(CO)_4(\eta^2\text{-diene})]$ complex **8** is suggested by its ^{13}C-NMR spectrum at $-70°$ in (D_8)toluene where 3 signals in a 1:2:1 ratio are detected for the CO ligands at 210 ppm. The site-specific complexation with C(4)=C(5) bond is apparent from a comparison of the ^{1}H-NMR spectrum of **8** with those of **4** and **9** (*cf. Table*). In **8**, H–C(3), which is located at the β-face and *cis* to the ethoxycarbonyl group, as well as H–C(5) are shifted to higher field by 0.72 and 2.03 ppm, whereas H–C(6) is only slightly affected. At the same time, the ^{13}C-signal of C(5) is shifted upfield by more than 50 ppm, whereas that of C(6) is shifted downfield by 6 ppm. The $[Fe(CO)_3(\eta^4\text{-diene})]$ complex **9** was readily identified by its formation from the structurally related complex **8**, its molecular weight (*m/z* 442 for M^+ including 3 CO), and consistent ^{13}C-NMR [16] and ^{1}H-NMR spectral data. Compared with **4**, H–C(5) as well as H–C(6) are shifted upfield by more than 1.3 ppm with H–C(3) only being slightly affected (*cf. Table*). Only a *s* is observed in the ^{13}C-NMR for the 3 CO ligands, even at $-70°$. Attempts to crystallize **9** or to replace one of its CO groups by $(C_6H_5)_3P$ have remained unsuccessful.

Table. *Selected ^{1}H-NMR Data* (δ [ppm]) *of* **4** *and* **8**–**10** *in* C_6D_6

	4	**8**	**9**	**10**
H–C(3)	5.67 (*dd*)	4.95 (*dd*)	5.38 (*dd*)	5.89 (*t*)
H–C(5)	6.26 (*s*)	4.23 (*s*)	4.92 (*d*)	4.45 (*s*)
H–C(6)	5.68 (*t*)	5.44 (*t*)	4.27 (*dd*)	4.12 (*s*)

The spectral data of **10** were not consistent with the formation of a stereoisomeric [Fe(CO)$_3$(diene)] complex. X-Ray analysis showed it to be a complex with a [Fe(CO)$_2$-(η^5-Cp)] moiety (*Fig.*)[6]. Surprisingly the unsubstituted allylic C(10)–C(13) bond at the

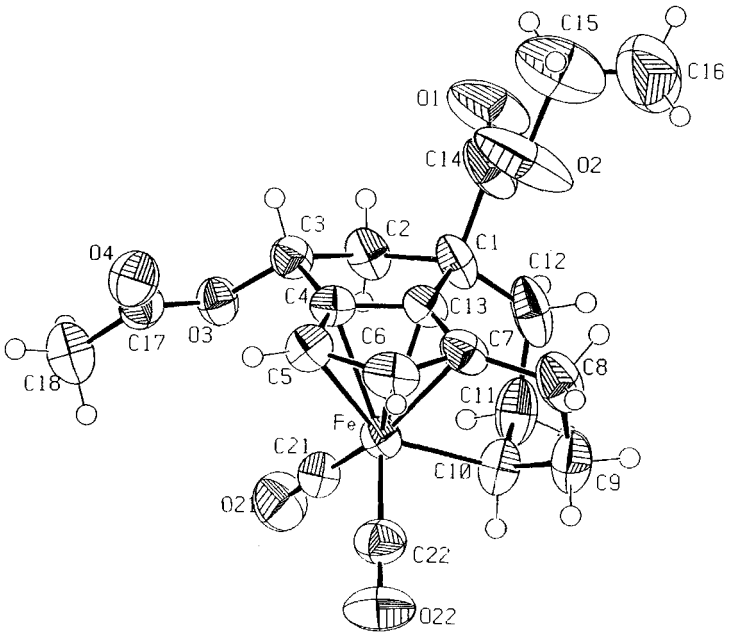


Figure. *X-Ray structure of* **10**. Selected bond lengths [Å] and angles [°] (arbitrary numbering): Fe–C(4) 2.110(4); Fe–C(5) 2.134(4), Fe–C(6) 2.091(4), Fe–C(7) 2.074(4), Fe–C(10) 2.063(5), Fe–C(13) 2.084(4), C(3)–C(4) 1.508(6), C(4)–C(13) 1.400(6), C(4)–C(5) 1.411(6), C(5)–C(6) 1.425(6), C(6)–C(7) 1.426(6); C(13)–C(1)–C(12) 112.9(4), C(13)–C(1)–C(14) 110.6(4), C(12)–C(1)–C(14) 108.1(4), C(13)–C(4)–C(3) 109.5(4).

[6]) *Crystal Structure Analysis of* **10**: $C_{20}H_{22}FeO_6$, M = 414.23; monoclinic, space group $P2_1/c$, a = 12.683(2), b = 8.416(1), c = 17.789(2) Å, b = 90.87(1)°, V = 1898.6(4) Å^3, Z = 4, D_{calc} = 1.449 g cm^{-3}, $F(000)$ = 864, I = 0.71073 Å, T 293(2) K, μ(MoK_α) 8.30 cm^{-1}. Data were collected for a crystal of size 0.61 × 0.53 × 0.23 mm, on a *Stoe-AED2* 4-circle diffractometer (graphite monochromated radiation) using $\omega/2\theta$ scans in the 2θ range 3–50°. Of the 3311 independent reflections measured, 2084 were considered observed ($I > 2\sigma(I)$). No absorption correction was applied. The structure was solved by direct methods using the program SHELXS-86 [17]. H-Atoms were included in calculated positions as riding atoms. The non-H atoms were refined anisotropically with full-matrix least-squares using the program SHELXL-93 [18]. Refinement converged at R = 0.053, wR_2 [18] = 0.126 for 2084 observed reflections. Residual density in the final difference map: max/min = 0.677/ – 0.520 e Å^{-3}. The *Figure* was drawn using the program XTAL_GX [19]. Full tables of atomic coordinates and bond distances and angles have been deposited with the *Cambridge Crystal Structure Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK.

central C-atom of **4** has been transformed into a Fe–CH bond with retention of configuration at C(10).

In view of the analogous reaction of spiro[4.4]nona-1,3-diene with $[Fe_2(CO)_9]$ which proceeded efficiently only in refluxing benzene [20] [21], the lability of $[Fe(CO)_4(\eta^2$-diene)] complexes in general [21], and the identification of $[Fe(CO)_4(\eta^2$-butadiene)] under matrix conditions at 12 K [22] [23], the formation and isolation of the complexes **8**–**10** at room temperature is remarkable. The $[Fe(CO)_2(Cp)]$ complex **10** is most likely formed *via* an α-face $[Fe(CO)_3(\eta^4$-diene)] complex by the migration of the C(10)–C(13) bond on the same side as the $Fe(CO)_3$ moiety and leading stereoelectronically favored to the observed conservation of the configuration at C(10). As we have no evidence for a bonding interaction between the ester group and the Fe in **9**, it is tempting to argue that the fact that **9** does not react to a β-face $[Fe(CO)_2(Cp)]$ complex corresponding to **10** might be due to the migratory aptitude of the C(1)–C(13) bond in the oxidative addition step which is reduced by the interaction with the ester group. In addition, the steric repulsion between the ester and the $Fe(CO)_3$ group might prevent the Fe to overlap with the C(1)–C(13) bond sufficiently well for reorganization. Further experiments are necessary before the impact of substituents on the reactivity of [5.5.5.5]fenestradienes containing a cyclopentadiene moiety towards $[Fe_2(CO)_9]$ can be understood.

Concluding Remarks. – The isolation of the complexes **8**–**10** under mild conditions and the side-specific reaction of **8** to **9** indicate that the topospecific reaction of substituted dienes like the fenestradiene **4** with $[Fe_2(CO)_9]$ depends on a variety of structural parameters. The unique structure of fenestranes leads to unusual reactions and, beyond the planarizing deformations, give insights into mechanistic features of a variety of reactions.

This work has generously been supported by the *Swiss National Science Foundation* and by the *Stipendienfonds der Basler Chemischen Industrie* with a stipend to *R. G.-G.* We thank Dr. *D. Monnier, Ciba-Geigy*, Marly, for the preparation of starting material and Dr. *C. Müller* for NMR investigations.

Experimental Part

General. See [24]. TLC: Silica gel plates *SIL G/UV*$_{254}$ (*Macherey & Nagel*); eluent *1* (hexane/AcOEt), *2* (hexane/Et_2O). Column chromatography (CC): silica gel from *J. T. Baker*. NMR Spectra: *Bruker-AC 300* (^{1}H 300 MHz; ^{13}C 75 MHz), *Bruker AM 500* (^{1}H 500 MHz; ^{13}C 125 MHz); st = stack, heavily overlapping signals; δ in ppm, J in Hz.

Ethyl rel-*(1*R,*2a*R,*4a*R,*8*R,*8a*S,*8b*R*)- and* rel-*(1*R,*2a*R,*4a*R,*8*S,*8a*S,*8b*R*)-1-(Acetyloxy)-1,2,2a,3,4,4a,5,6,8,8a-decahydro-8-hydroxypentaleno[1,6-cd]pentalene-2a-carboxylate* (**2a** and **2b**, resp.). To a soln. of the enone **1** [3] (300 mg, 0.94 mmol) in MeOH (9 ml) was added $CeCl_3 \cdot 7\,H_2O$ (356.1 mg, 0.96 mmol) under Ar at r.t. After 0.5 h, $NaBH_4$ (38 mg, 1.0 mmol) was added in portions. The mixture was stirred at r.t. for 2 h, then quenched with cold H_2O and dil. HCl soln. The resulting mixture was poured into AcOEt, washed with H_2O and brine, dried ($MgSO_4$), and evaporated. CC (silica gel, *1* 1:2) yielded **2a** (102.3 mg, 44%) and **2b** (128.8 mg, 56%), both as light-yellow oils.

2a: R_f (*1*, 1:1) 0.41. IR: 3460 (br.), 1720, 1250. ^{1}H-NMR: 1.27 (*t*, 3 H); 1.61–177 (st, 2 H); 1.89–1.99 (st, 2 H); 2.05 (*s*, 3 H); 2.09–2.22 (st, 3 H); 2.27–2.37 (*m*, 1 H); 2.47–2.58 (st, 2 H); 2.94 (*dd*, J = 15.0, 9.0, 1H); 3.09 (*d*, 1 H); 4.13 (*q*, 2 H); 4.73–4.79 (*m*, 1 H); 5.47–5.52 (*m*, 1 H); 5.47 (*m*, 1 H). ^{13}C-NMR: 14.19 (*q*); 21.38 (*q*); 25.90 (*t*); 33.15 (*t*); 34.02 (*t*); 36.27 (*t*); 46.19 (*t*); 48.25 (*d*); 61.20 (*t*); 61.90 (*d*); 63.96 (*s*); 77.21 (*d*); 79.46 (*d*); 81.48 (*s*); 123.67 (*d*); 157.47 (*s*); 170.86 (*s*); 176.47 (*s*). GC-MS: 260 (93, $[M - 60]^+$), 242 (19), 232 (50), 214 (26), 203 (13), 186 (71), 175 (11), 169 (51), 159 (46), 147 (29), 141 (22), 129 (50), 117 (45), 105 (36), 91 (48), 43 (100).

2b: R_f (*1*, 1:1), 0.28. IR: 3545 (br.), 1720, 1260. ^{1}H-NMR: 1.24 (*t*, 3 H); 1.55–1.62 (*m*, 1 H); 1.66–1.73 (st, 2 H); 1.94 (*dd*, J = 9.0, 6.0, 1 H); 2.02–2.21 (st, 4 H); 2.08 (*s*, 3 H); 2.30–2.43 (st, 3 H); 2.65 (*dd*, J = 9.0, 6.0,

1 H); 3.07 (*m*, 1H); 4.08 (*q*, 2 H); 5.07 (*m*, 1 H); 5.23–5.31 (st, 2 H). ^{13}C-NMR: 14.25 (*q*); 21.33 (*q*); 26.55 (*t*); 33.28 (*t*); 33.67 (*t*); 34.66 (*t*); 42.59 (*t*); 48.20 (*d*); 60.64 (*t*); 62.88 (*d*); 72.00 (*d*); 80.84 (*d*); 81.50 (*s*); 87.34 (*d*); 122.84 (*d*); 154.03 (*s*); 171.97 (*s*); 174.78 (*s*). GC-MS: 242 (76, $[M-78]^+$), 213 (21), 201 86), 188 (14), 169 (100), 153 (23), 141 (41), 129 (48), 115 (36), 103 (11), 43 (65).

Ethyl rel-*(1*R,*2a*R,*4a*S,*8a*R,*8b*R*)-1-(Acetyloxy)-1,2,2a,3,4,4a,5,8a-octahydropentaleno[1,6-*cd*]pentalene-2a-carboxylate* (**3**) *and Ethyl* rel-*(1*R,*2a*R,*4a*R,*8b*S*)-1-(Acetyloxy)-1,2,2a,3,4,4a,5,6-octahydropentaleno[1,6-*c*]-2a-carboxylate* (**4**). Heating of **2a** or **2b** with 6.3 mol-equiv. of $HC(OMe)_2NMe_2$ in xylene for 48 h under anh. conditions yielded **3**/**4**. CC with (*1* 2:1) gave 21% of **3** and 46% of **4**.

3: R_f (*2*, 1:1) 0.4. IR: 1720, 1180, 1090, 1020. ^{1}H-NMR: 1.19 (*t*, 3 H); 1.71–1.82 (st, 3 H); 2.07 (*s*, 3 H); 2.04–2.18 (*m*, 1 H); 2.63–2.69 (st, 2 H); 2.76–2.91 (st, 3 H); 2.94–2.96 (*m*, 1 H); 4.01 (*q*, 2 H); 5.20–5.24 (*m*, 1 H); 5.31 (*m*, 1 H); 6.04 (*dd*, 1 H); 6.15 (*dd*, 1 H). ^{13}C-NMR: 13.99 (*q*); 21.22 (*q*); 28.98 (*t*); 36.80 (*t*); 42.29 (*t*); 43.75 (*t*); 51.84 (*d*); 60.44 (*t*); 61.70 (*d*); 64.47 (*s*); 79.48 (*d*); 82.43 (*s*); 117.81 (*d*); 127.75 (*d*); 139.82 (*d*); 153.53 (*s*); 170.51 (*s*); 175.50 (*s*). GC-MS: 302 ($5M^+$), 242 (82), 213 (22), 188 (13), 169 (100), 153 (28), 141 (41), 129 (51), 115 (39).

4: R_f (*1*, 1:1) 0.65. IR: 1720, 1250, 1100. ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz): 1.31 (*t*, *J* = 7.0, 3 H); 1.89–1.97 (st, 2 H); 2.10 (*s*, 3 H); 2.16 (*m*, 1 H); 2.45 (*m*, 1 H); 2.60 (*m*, 1 H); 2.69 (*m*, 1 H); 2.82 (*m*, 1 H); 2.98 (*m*, 1 H); 3.05 (*m*, 1 H); 3.19 (*m*, 1 H); 3.86 (*dd*, *J* = 15.1, 7.4, 1 H); 4.26 (*m*, 2 H); 5.94 (*dd*, *J* = 7.2, 1.6, 1 H); 6.02 (*s*, 1 H); 6.55 (*s*, 1 H). ^{13}C-NMR ($C_6D_5CD_3$, 125 MHz): 14.14 (*q*); 20.62 (*q*); 25.19 (*t*); 33.99 (*t*); 37.16 (*t*); 39.48 (*t*); 43.41 (*d*); 48.88 (*t*); 57.12 (*s*); 60.20 (*t*); 69.87 (*d*); 83.13 (*s*); 124.60 (*d*); 131.37 (*d*); 154.53 (*s*); 161.49 (*s*); 169.27 (*s*); 172.68 (*s*). GC-MS: 302 ($13M^+$), 259 (47), 242 (46), 213 (25), 186 (51), 169 (100), 141 (50), 128 (67), 115 (46), 91 (19).

Tetracarbonyl{(8,8a-η)[ethyl rel-*(1*R,*2a*R,*4a*R,*8*R,*8a*R,*8b*R*)-1-(acetyloxy)-1,2,2a,3,4,4a,5,6-octahydropentaleno[1,6-*cd*]pentalene-2a-carboxylate]}iron* (**8**), *Tricarbonyl{(6a,7,8,8a-η)-[ethyl* rel-*(1*R,*2a*R,*4a*S,*6a*R,7S,*8*S,*8a*R,*8b*S*)-1-(acetyloxy)-1,2,2a,3,4,4a,5,6-octahydropentaleno[1,6-*cd*]pentalene-2a-carboxylate]}iron* (**9**), *and Dicarbonyl{(1,2,2a,9a,9b-η,κC^7)-[*rel-*(1*R,*2*S,*2a*S,*3*R,*4a*S,*7*S,*9a*R,*9b*R*)-3-(Acetyloxy)-4a-(ethoxycarbonyl)-1*H-*cyclooct[cd]pentalen-1-ylium-7-yl]}iron* (**10**). At r.t. **4** (100 mg, 0.33 mmol) was treated with a large excess of $[Fe_2(CO)_9]$ in benzene (15 ml) under Ar for 17 h. The resulting dark-green mixture was filtered through *Celite* and rinsed with Et_2O. The filtrate was evaporated to give, after flash CC and HPLC (*1*, 10:1), **8** (79 mg, 54%), **9** (14 mg, 10%), and **10** (20 mg, 14%) as yellow oils.

8: R_f (*1*, 8:1) 0.32. IR: 1960, 1720, 1245 (*s*). ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz, −30°): 0.91 (br. *s*, 3 H); 1.77 (st, 2 H); 1.90 (*m*, 1 H); 2.12 (*d*, *J* = 14.4, 1 H); 2.19 (*s*, 3 H); 2.29 (*m*, 1 H); 2.46 (st, 3 H); 2.71 (*m*, 1 H); 3.06 (*m*, 1 H); 3.77 (*dd*, *J* = 14.4, 7.2, 1 H); 4.17 (*m*, 2 H); 4.48 (*s*, 1 H); 5.23 (br. *s*, 1 H); 5.72 (*s*, 1 H). ^{13}C-NMR ($C_6D_5CD_3$, 125 MHz, −30°): 210.22 (br. *s*); 172.92 (*s*); 168.99 (*s*); 150.31 (*s*); 130.34 (*d*); 87.78 (*s*); 86.07 (*s*); 80.42 (*d*); 72.16 (*d*); 63.05 (*s*); 60.32 (*t*); 48.35 (*d*); 47.17 (*t*); 36.10 (*t*); 35.20 (*t*); 33.80 (*t*); 24.71 (*t*); 20.27 (*q*); 13.99 (*q*). MS: 442 (8, $[M-CO]^+$), 414 (4, $[M-2CO]^+$), 386 (17, $[M-3CO]^+$), 358 (97, $[M-4CO]^+$), 298 (100), 285 (33), 254 (45), 244 (17), 226 (19), 169 (45), 153 (12), 141 (22), 129 (24), 115 (18). HR-MS: 440.07590 ($[M-CO]^+$; calc. 440.076165).

9: R_f (*1*, 8:1) 0.21. IR: 1980, 1960, 1720, 1710. ^{1}H-NMR ($C_6D_5CD_3$ 500 MHz): 1.36 (*t*, *J* = 7.4, 3 H); 1.58–1.64 (st, 2 H); 1.81 (*dd*, *J* = 12.2, 6.3, 1 H); 1.91–2.04 (st, 2 H); 2.23 (*m*, 1 H); 2.39 (*m*, 1 H); 2.46 (*s*, 3 H); 2.59 (*m*, 1 H); 2.93 (*m*, 1 H); 3.26 (*m*, 1 H); 3.45 (*dd*, *J* = 14.8, 6.9, 1 H); 4.26 (*m*, 2 H); 4.65 (*s*, 1 H); 5.25 (*s*, 1 H); 5.63 (*d*, *J* = 6.9, 1 H). ^{13}C-NMR (C_6D_6, 125 MHz): 212.22 (*s*); 173.24 (*s*); 168.74 (*s*); 110.22 (*s*); 90.98 (*s*); 84.21 (*d*); 75.21 (*d*); 74.21 (*d*); 68.37 (*s*); 67.59 (*s*); 60.16 (*t*); 47.04 (*d*); 41.57 (*t*); 38.67 (*t*); 36.39 (*t*); 31.03 (*t*); 27.08 (*t*); 19.96 (*q*); 13.96 (*q*). MS: 442 ($13M^+$), 386 (20, $[M-2CO]^+$), 358 (100, $[M-3CO]^+$), 298 (85), 285 (37), 254 (40), 244 (12), 226 (19), 169 (22), 129 (14). HR-MS: 440.07581 (calc. 440.076165).

10: The oil solidified at 0° and was recrystallized from pentane at 0°. M.p. 90–92°. R_f (*1*, 8:1) 0.28. IR: 1995, 1935, 1715. ^{1}H-NMR (C_6D_6, 300 MHz): 0.86 (*t*, *J* = 7.0, 3 H); 1.61 (*d*, *J* = 14.0, 1 H); 1.80 (*s*, 3 H); 1.71–1.90 (st, 2 H); 1.99 (br. *d*, *J* = 14.0, 1 H); 2.19 (*dd*, *J* = 13.0, 7.5, 1 H); 2.32 (st, 2 H); 2.42 (*m*, 1 H); 2.70 (*m*, 1 H); 3.02–2.92 (st, 2 H); 3.87 (*q*, *J* = 7.0, 2 H); 4.13 (*d*, *J* = 2.2, 1 H); 4.46 (*d*, *J* = 2.2, 1 H); 6.00 (*t*, *J* = 7.5, 1 H). ^{13}C-NMR (C_6D_6, 125 MHz): 219.47 (*s*); 215.59 (*s*); 174.71 (*s*); 169.92 (*s*); 114.04 (*s*); 111.16 (*s*); 107.81 (*s*); 90.27 (*d*); 70.78 (*d*); 67.99 (*d*); 61.24 (*t*); 54.06 (*t*); 47.92 (*s*); 43.02 (*t*); 34.90 (*t*); 32.07 (*d*); 30.27 (*t*); 24.48 (*t*); 20.16 (*q*); 13.86 (*q*). MS: 414 ($5M^+$), 386 (13, $[M-CO]^+$), 358 (71, $[M-2CO]^+$), 298 (100), 285 (36), 260 (10), 254 (48), 244 (26), 226 (24), 169 (26). HR-MS: 412.08084 (calc. 412.081251).

REFERENCES

[1] W. Luef, R. Keese, in 'Advances in Strain in Organic Chemistry', Ed. B. Halton, JAI Press, Greenwich, Ct., 1993, Vol. 3, p. 711.

[2] M. Thommen, P. Gerber, R. Keese, *Chimia* **1991**, *45*, 21.

[3] M. Thommen, R. Keese, *Helv. Chim. Acta* **1996**, *79*, 461.
[4] M. Thommen, R. Keese, *Synlett* **1997**, accepted for publication.
[5] P. A. Wender, T. M. Moore, M. A. deLong, *Tetrahedron Lett.* **1996**, *37*, 7687.
[6] a) R. Keese, in 'Organic Synthesis: Modern Trends', Ed. O. Chizhov, Blackwell Scientific Publications, Oxford, 1987, p. 43; b) R. Keese, W. Luef, J. Mani, S. Schüttel, M. Schmid, C. Zhang, in 'Strain and Its Implications in Organic Chemistry', Ed. A. de Meijere and S. Blechert, Kluwer Academic Publ., Dordrecht, 1988, p. 283; c) M. Schmid, Ph. D. Thesis, University of Bern, 1987.
[7] G. Büchi, M. Cushman, H. Wüest, *J. Am. Chem. Soc.* **1974**, *96*, 5563.
[8] K.-K. Chan, G. Saucy, *J. Org. Chem.* **1977**, *42*, 3828.
[9] J. D. Cox, G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London, 1970, p. 592.
[10] W. F. Maier, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 1891; A. B. McEwen, P. v. R. Schleyer, *ibid.* **1986**, *108*, 3951.
[11] J. Wang, M. Thommen, R. Keese, *Acta Crystallogr., Sect. C* **1996**, 2311.
[12] H. Kukuk, E. Proksch, A. de Meijere, *Angew. Chem.* **1982**, *94*, 304; *ibid. Int. Ed.* **1982**, *21*, 306; *ibid. Suppl.* **1982**, 696.
[13] HyperChem 3 for Windows', Autodesk, Inc., 1993.
[14] R. Grée, *Synthesis* **1989**, 341.
[15] A. J. Deeming, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, Vol. 4, Chapt. 31.3.
[16] W. A. Donaldson, in 'Comprehensive Organometallic Chemistry' II, Ed. L. S. Hegedus, Pergamon Press, Oxford, 1995, Vol. 12, 623.
[17] G. M. Sheldrick, 'SHELXS-86', *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[18] G. M. Sheldrick, 'SHELXL-93'. Program for Crystal Structure Refinement 1993, Universität Göttingen, Germany.
[19] S. Hall, D. du Boulay, XTAL-GX 1995, Hall & du Boulay, University of Western Australia, Australia.
[20] B. F. Hallam, P. L. Pauson, *J. Chem. Soc.* **1958**, 646.
[21] P. Eilbracht, P. Dahler, *Chem. Ber.* **1980**, *113*, 542.
[22] G. Ellerhorst, W. Gerhartz, F.-W. Grevels, *Inorg. Chem.* **1980**, *19*, 67.
[23] S. T. Astley, M. P. V. Churton, R. B. Hitam, A. J. Rest, *J. Chem. Soc., Dalton Trans.* **1990**, 3243.
[24] C. Boss, R. Keese, *Helv. Chim. Acta* **1996**, *79*, 2164.