183. Synthesis of Enantiomerically Pure Carbohydrate-Derived Annulated Cyclopentadienes and Ferrocenes

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The cyclopentadienes **3a/b/c**, **8b/c**, **12a/b/d**, and **16a/b/d** were prepared as mixtures of regioisomers from the D-mannitol-derivatives **1**, **6**, **10**, and **14** and transformed into the ferrocenes **17**, **18**, and **19** (73%; 38:17:45), **23**, **24**, and **25** (70%; 6:42:52), **26** (31%), and **27** (27%), respectively. Deprotection of **17–19** with HCl/MeOH gave the H_2O-soluble ferrocenes **20–22**; chloromercuration and iodination of **17** *via* **29** led to the C_2-symmetric diiodoferrocene **30**. The mono(chloromercurio) derivative **28**, obtained as a by-product, was also transformed into **29**. The structure of the ferrocenes **18** and **19**, and of the bis(chloromercurio)ferrocene **29** has been established by X-ray analysis. The starting cyclopentadienes **3** were obtained in 50% yield from **1** by dialkylation of CpNa, followed by thermolysis of the spiro-annulated **2**. Similarly, dimesylate **6** (from **4**) gave the spiro-annulated diene **7** and the annulated dienes **8** in about equal amounts; thermolysis transformed **7** into **8** (62%). The dienes **12** were prepared in 15% yield from the ditriflate **10** *via* **11**, the dimesylate **9** proving insufficiently reactive, and the dienes **16** (49%) from **14** *via* **15**.

Introduction. – Enantiomerically pure cyclopentadiene-derived metallocenes have been widely used in asymmetric reactions, either as catalysts, or in stoichiometric amounts [1–3]. Reactions catalyzed by transition-metal complexes derived from enantiomerically pure difunctional ferrocenes include cross-coupling [4], allylic substitution [5], an asymmetric aldol-type reaction of isocyanocarboxylates [6], hydrogenation [7–9] and hydrosilylation [10] of alkenes and ketones, *Michael* additions [11], intramolecular asymmetric *Heck*-type reactions of alkenyl iodides [12], the hydroboration of styrene [8], and the alkylation of carbonyl compounds with R_2Zn [13].

Novel enantiomerically pure cyclopentadienyl ligands are required to improve the properties of metallocenes, and annulated cyclopentadienes have received considerable attention. They have been synthesized, *e.g.*, by a double *Wittig* olefination of camphorquinone [14], by addition of a three-carbon fragment to camphor followed by ring closure [15–19], by a *Skattebøl* rearrangement of vinyl cyclopropane [18–20], by the bis-alkylation of cyclopentadiene [1] [15] [16] [21], and by *Nazarov* cyclizations [22]. Carbohydrates commend themselves as starting materials for the synthesis of enantiomerically pure ligands: they are structurally diverse, can easily be transformed to derivatives, and may lead to H_2O-soluble catalysts. However, only a few enantiomerically pure cyclopentadienes connected to a carbohydrate-derived moiety by C–C bonds have been prepared [15] [16] [23], among them only one simple carbohydrate-derived annulated cyclopentadiene [15] [16].

We have reported the preparation of a number of enantiomerically pure C_1-symmetric *C*-glycosylcyclopentadienes from hemiacetals and their transformation into ferrocenes

and into a titanocene [24], and we now describe the synthesis of novel C_1- or C_2-symmetric, carbohydrate-derived annulated cyclopentadienes and their transformation into substituted ferrocenes.

Results and Discussion. – 1. *Annulated Cyclopentadienes.* We have applied the method of *Halterman* and coworkers [1] [15] [16] [21], dialkylation of cyclopentadiene with primary 1,4-diols, to the synthesis of annulated cyclopentadienes possessing a side chain at the α-position, by alkylating cyclopentadiene with carbohydrate-derived 1,4-diols in which at least one OH group is secondary.

The dimesylate **1** [25], prepared from 2,3:5,6-di-*O*-isopropylidene-D-mannitol, was treated with cyclopentadienylsodium (CpNa) and NaH. This led mostly to the spiro-annulated cyclopentadiene **2** (63%) and to small amounts (5%) of the annulated cyclopentadiene **3a** (*Scheme 1*). Spiro-annulation is here favorable, while it is not observed in the analogous reaction of a related tartrate [15]. The S_N2-type displacement of both leaving groups by the cyclopentadienyl moiety leads to an inverted configuration at C(i)[1]) of the spiro-compound **2**, as evidenced by the X-ray analyses of the ferrocenes **18** and **19** (see below). Thermolysis of the spiro-diene **2** in toluene at 240° resulted in a [1,5]-sigmatropic alkyl shift [26] followed by [1,5]-sigmatropic H-shifts to yield the annulated cyclopentadienes **3a**/**b**/**c** 2:1:1 (71%), as a mixture of three out of the five possible regioisomers. Their ratio was determined by integration of the signals of the olefinic H-atoms of each isomer in the ^{1}H-NMR spectrum of the crude product. Flash chromatography separated **3a** from **3b**/**c**; pure **3b** and **3c** were obtained by prep. HPLC.

O-Isopropylidene-protected titanocenes are acid-labile [24]. For this reason, we have also prepared the *O*-methylated analogues **8** of **3**. The tetra-*O*-methyl-D-mannofuranose **4** [27] was reduced by $NaBH_4$ to the diol **5** (84%) and dimesylated to **6** (99%). Alkylation of **6** with CpNa and NaH afforded the spiro-annulated cyclopentadiene **7** (36%) and the annulated, regioisomeric cyclopentadienes **8b**/**c** 45:55 (42%). Obviously, the tetra-*O*-methyl derivative **6** forms the six-membered ring much more readily than the di-*O*-isopropylidene derivative **1**. Thermolysis of **7** in toluene at 230° gave again the two cyclopentadienes **8b**/**c** 45:55 (62%, ratio determined by ^{1}H-NMR spectroscopy). Pure samples of **8b** and **8c** were obtained by prep. HPLC. They isomerized in $CDCl_3$ solution over a period of several days to mixtures **8b**/**c**.

To avoid the formation of diastereoisomeric metallocenes, we have also prepared annulated cyclopentadienes from a C_2-symmetric 1,4-diol possessing two secondary OH groups. Alkylation of CpNa by the mesylate **9** [28] failed, but the triflate **10** [29] reacted with CpNa (or CpLi) and excess NaH, yielding 27% of the C_2-symmetric spiro-annulated cyclopentadiene **11** besides elimination products. No trace of the annulated cyclopentadienes **12** was observed. Thermolysis of **11** at 240° afforded a mixture of the three regioiso-

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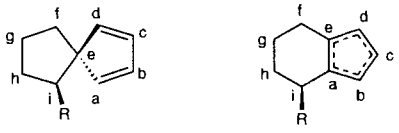
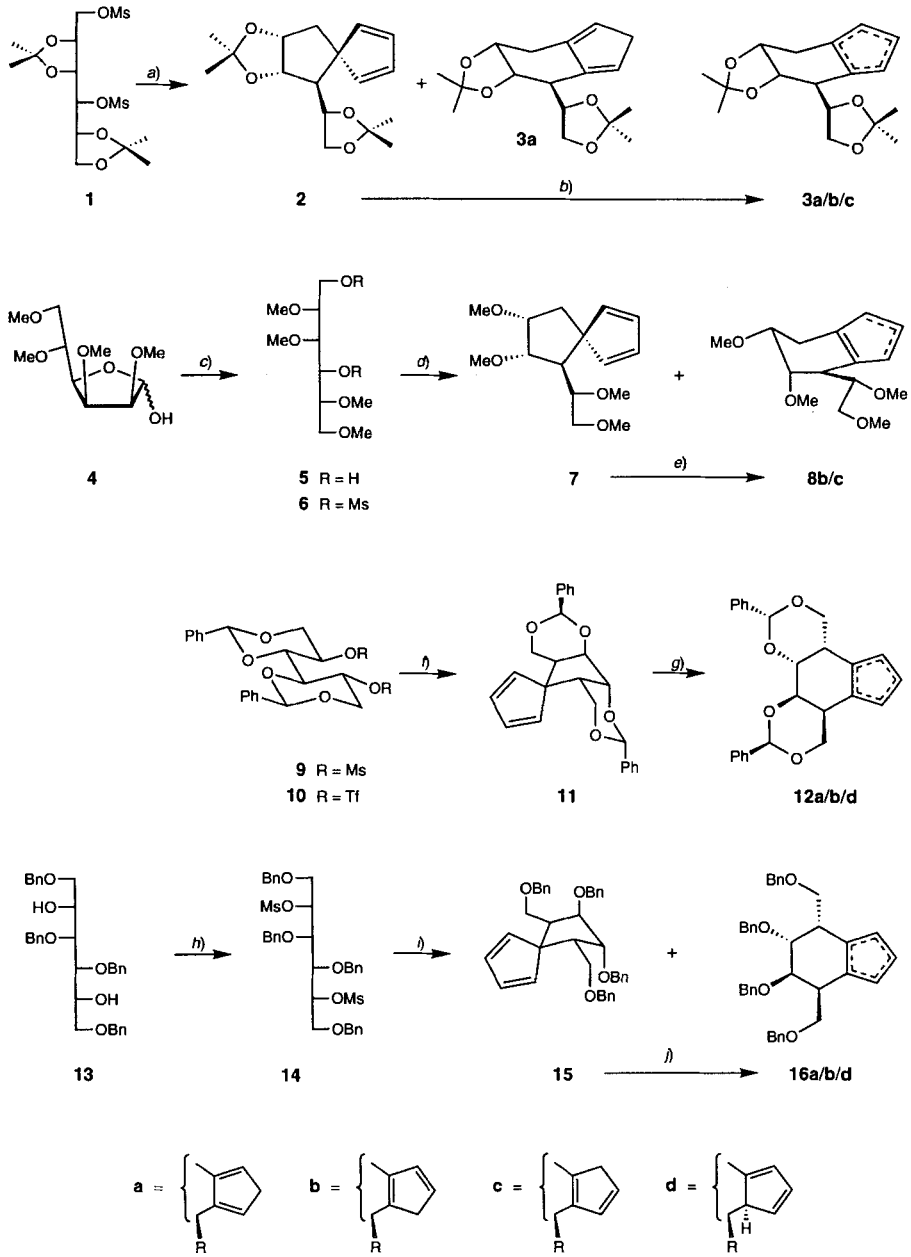
[1]) In the *General Part* and in the *Tables*, the C-atoms of the ring skeleton of the spiro[4.4]nonadiene and the tetrahydroindene moieties are marked with a–i in the following manner:



Scheme 1



a) CpNa, NaH, THF/HMPA; 63% of **2** and 5% of **3a**. *b*) Toluene, 240°; 71%. *c*) $NaBH_4$, EtOH; 84% of **5**; MsCl, Et_3N, CH_2Cl_2; 99% of **6**. *d*) CpNa, NaH, THF; 36% of **7** and 42% of **8b/c**. *e*) Toluene, 230°; 62%. *f*) As *a*); 27% from **10**. *g*) As *b*); 57%. *h*) MsCl, Et_3N, CH_2Cl_2; 94%. *i*) CpNa, THF/HMPA; 40% of **15** and 23% of **16a/b/d**. *j*) As *e*); 64%.

meric cyclopentadienes **12b**/**d**/**a** 86:8:6 (57%). While **12d** was separated from **12a**/**b** by flash chromatography, **12a** and **12b** could not be separated even by HPLC. Similarly to **8**, $CDCl_3$ solutions of these samples isomerized slowly at room temperature.

The less strongly hindered *O*-benzyl-protected dimesylate **14** [30] was prepared in a improved yield of 94% by treating **13** with MsCl and Et_3N. As expected, **14** reacted with CpNa, to yield the C_2-symmetric spiro-annulated cyclopentadiene **15** in 40% and the regioisomeric cyclopentadienes **16b**/**a**/**d** 90:5:5 in 23% yield. Addition of NaH had to be avoided. Again, the tetra-*O*-benzyl derivative **14** formed substantial amounts of six-membered products, while the di-*O*-benzylidene triflate **10** led only to the five-membered **11**. Thermolysis of **15** afforded the same cyclopentadienes **16b**/**a**/**d** 69:23:8 (64%), but in a different proportion. The isomers **16b**/**a**/**d** were separated by flash chromatography.

Table 1. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of* **2**, **3a–c**, **7**, **8b,c**, **11**, **12a,b,d**, **15**, *and* **16a,b,d**[l])

	2	**3a**	**3b**	**3c**	**7**	**8b**	**8c**
H–C(a)	6.52–6.47[a])	–	–	–	6.16[a])[d])	–	–
H–C(b)	6.27–6.22	6.07	3.11, 3.00[c])	6.53[d])	6.44–6.36[b])[d])	3.09, 2.80[c])	6.37[d])
H–C(c)	6.27–6.22	3.04, 2.95[c])	6.35[d])	6.29[d])	6.44–6.36[b])[d])	6.30[d])	6.23[d])
H–C(d)	6.34–6.30[a])	6.28	6.35[d])	2.95, 2.88[c])	6.12[a])[d])	6.30[d])	2.87, 2.87[c])
H_A–C(f)	2.04	3.02–2.94	2.78	2.82	1.86	2.60–2.54	2.64
H_B–C(f)	1.93	2.54	2.55	2.56	1.80	2.60–2.54	2.52
H–C(g)	4.80	4.37	4.46	4.49	3.93	3.69–3.62	3.61
H–C(h)	4.63	4.12	4.16	4.26	3.78	3.69–3.62	3.69
H–C(i)	2.58	2.79	2.87–2.80	2.85–2.81	2.66	3.01–2.97	3.04–2.95
$J(f_A,f_B)$	13.3	14.4	17.4	17.4	13.0	[e])	17.0
$J(f_A,g)$	5.0	5.9	6.6	6.5	3.8	[e])	5.8
$J(f_B,g)$	6.5	7.5	4.0	3.7	4.4	[e])	9.0
J(g,h)	6.8	7.1	5.9	6.2	4.6	[e])	2.4
J(h,i)	5.1	7.1	4.1	3.6	9.4	[e])	2.4

	11	**12a**	**12b**	**12d**	**15**	**16a**	**16b**	**16d**
H–C(a)	6.29[d])	–	–	3.71	6.20[d])	–	–	2.88
H–C(b)	6.78[d])	6.37	3.25, 3.03[c])	6.62[d])	6.28[d])	6.14	2.92, 2.92	6.44[d])
H–C(c)		3.12–3.08	6.46[d])	6.57[d])		2.89	6.30[d])	6.38[d])
H–C(d)			6.64[d])	6.48			6.52[d])	6.00
H–C(f)	2.91	2.88–2.83	2.75[a])	2.80	3.05	3.34–3.23	3.26–3.15	3.30–3.21
H–C(g)	4.55	4.29	4.49[b])	4.42[a])	4.22	4.07	4.07–3.98	4.04[a])
H–C(h)			4.46[b])	4.21[a])			4.07–3.98	3.89[a])
H–C(i)			2.69[a])	1.42			3.26–3.15	1.91–1.78
J(f,g)	3.4	1.8	[e])	2.8	4.0	2.8	[e])	3.6
J(g,h)			[e])	2.8			[e])	3.6
J(h,i)			[e])	2.8			[e])	3.6
J(a,i)	–	–	–	12.1	–	–	–	11.0

[a])[b]) Assignment may be interchanged. [c]) J_{gem} = 24.0 (**3a**, **3b**), 22.0 (**3c**), and 23.0 Hz (**8b**, **12b**). Not determined for **8c**. [d]) J_{vic} = 5.2 (**7**), 5.4 (**3c**, **8c**, **12b**, **12d**, **16b**, **16d**), 6.2 (**8b**, **15**), and 6.5 Hz (**11**). H–C(c) and H–C(d) of **3b** are isochronous. [e]) Not determined.

Table 2. *Selected* ^{13}C*-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *of* **2**, **3a**, **7**, **8b**,**c**, **11**, **12b**, **15**, *and* **16b**[1])

	2	**3a**	**7**	**8b**	**8c**	**11**	**12b**	**15**	**16b**
C(a)	143.03[a])	141.86[a])	146.72[a])	137.35[a])	138.07[a])	144.00	138.35[a])	142.43	137.39[a])
C(b)	130.70[b])	125.57[b])	127.99[b])	43.07	133.73[b])	129.28	41.21	129.39	41.66
C(c)	128.36[b])	41.30	126.94[b])	132.26[b])	130.79[b])		131.35[b])		131.37[b])
C(d)	138.12[a])	127.96[b])	142.78[a])	133.46[b])	43.08		131.56[b])		132.08[b])
C(e)	65.01	141.31[a])	59.13	136.06[a])	135.48[a])	63.58	137.77[a])	62.58	136.83[a])
C(f)	39.03	29.52	34.07	26.75	27.19	40.53	32.41[c])	45.82	37.77[c])
C(g)	80.18[c])	76.57[c])	80.01[c])	78.52[c])	78.08[c])	82.23	75.09[d])	81.82	74.21[d])
C(h)	83.37[c])	77.08[c])	83.78[c])	81.12[c])	81.56[c])		74.73[d])		74.12[d])
C(i)	52.66	43.35	47.85	42.27	41.29		31.38[c])		36.68[c])

[a])[b])[c])[d]) Assignment may be interchanged.

That **2**, **7**, **11**, and **15** are spiro[4.4]nona-1,3-dienes is indicated by NMR signals of four olefinic H between 6.1 and 6.8 ppm (*Table 1*), of four *d* for the olefinic C (C(a) and C(d) between 138.1 and 146.8 ppm, C(b) and C(c) between 126.9 and 130.7 ppm; *Table 2*), and a *s* for the spiro-C between 59.1 and 65.1 ppm. The signals for CH_2(f) of **2** and **7** (^{1}H-NMR: *dd* at 2.04 and 1.93 ppm (J_{gem} = 13.3 Hz; **2**) and at 1.86 and 1.80 ppm (J_{gem} = 13 Hz; **7**); ^{13}C-NMR: *t* at 39.03 (**2**) and 34.07 ppm (**7**)), CH(i) of **2** and **7** (^{1}H-NMR: *t* at 2.58 (J = 5.1 Hz; **2**) and *dd* at 2.66 ppm (J = 9.3, 4.0 Hz; **7**); ^{13}C-NMR: *d* at 52.66 (**2**) and 47.85 ppm (**7**)), and of CH(f) of **11** and **15** (^{1}H-NMR: *t* at 2.91 (J = 3.4 Hz; **11**) and *dt* at 3.05 ppm (J = 10.3, 4.0 Hz; **15**); ^{13}C-NMR: *d* at 40.53 (**11**) and 45.82 ppm (**15**)) are shifted upfield.

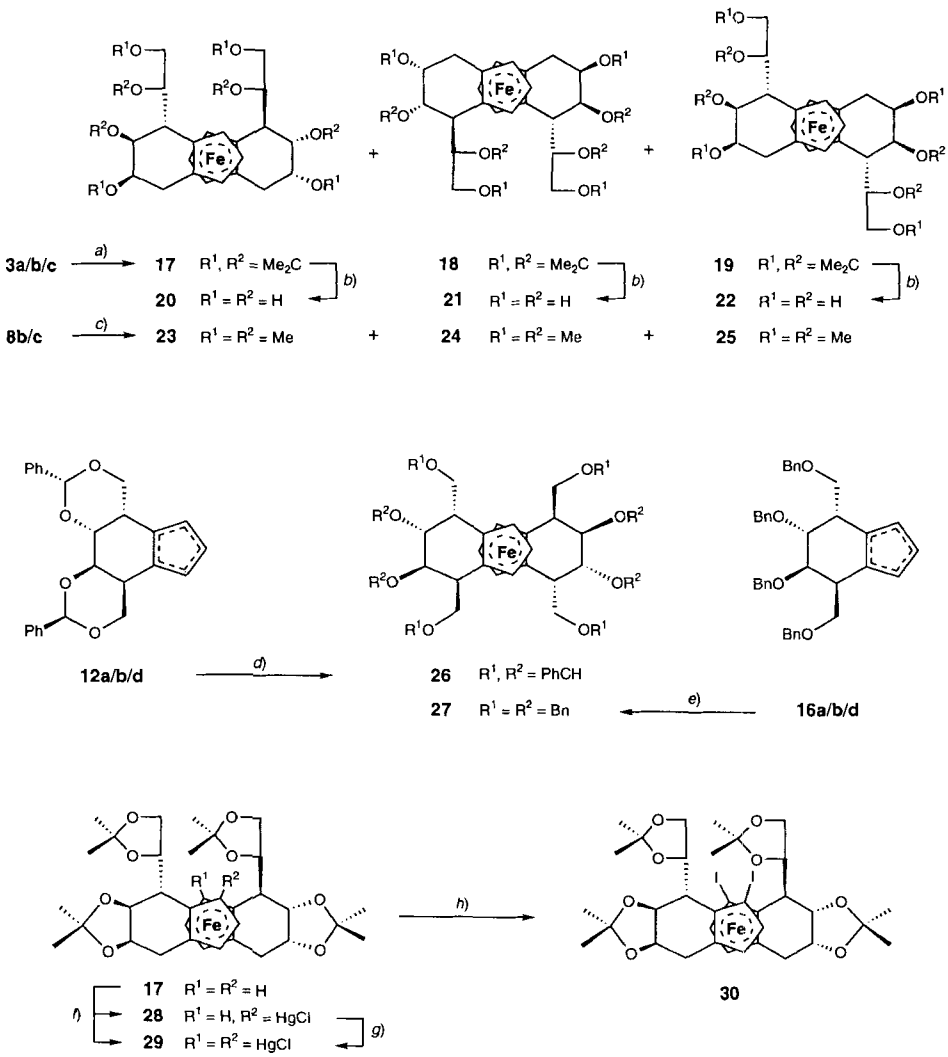
The 4,5,6,7-tetrahydro-1*H*- and -2*H*-indene structure of **3a**/**b**/**c** and **8b**/**c** is revealed by signals for two olefinic H and a CH_2 group exhibiting the characteristic large J_{gem} of 22–24 Hz (*Table 1*; *cf.* [24]). In **a**, the CH_2 group is inserted between the olefinic CH groups, as shown by the absence of a vicinal coupling of *ca.* 6 Hz between these CH. The two broad signals at 6.28 and 6.07 ppm in the ^{1}H-NMR spectrum of **3a** show only small vicinal and long-range couplings. For **b** and **c**, one expects broad *d* of the olefinic H-atoms. Also, the neighborhood of the doubly allylic CH_2 group of **b** to the asymmetric centre C(i) should lead to a large $\Delta\delta$ for the CH_2 group and a small $\Delta\delta$ for the olefinic H-atoms; for **c**, one expects a small $\Delta\delta$ for the CH_2 group and a large $\Delta\delta$ for the olefinic H-atoms. Large $\Delta\delta$ values are indeed observed for the CH_2 groups of **3b** and **8b** (0.11 and 0.29 ppm, resp.) and for the olefinic H-atoms of **3c** and **8c** (0.24 and 0.14 ppm, resp.) and small $\Delta\delta$ values for the CH_2 groups of **3c** and **8c** (0.07 and < 0.02 ppm) and for the olefinic H of **3b** and **8b** (< 0.02 ppm; *Table 1*). In agreement with this assignment, the ^{13}C-NMR spectra of **3a**, **8b**, and **8c** exhibit two *s* (**3a** at 141.86 and 141.31 ppm, **8b** at 137.35 and 136.06 ppm, **8c** at 138.07 and 135.48 ppm), two *d* (**3a** at 127.96 and 125.57 ppm, **8b** at 133.46 and 132.26 ppm, **8c** at 133.73 and 130.79 ppm), and a *t* (**3a** at 41.30 ppm, **8b** at 43.07 ppm, **8c** at 43.08 ppm) for the cyclopentadiene moiety (*Table 2*). As expected, the shift values of the 1*H*-indenes **8b** and **8c** are similar and differ more strongly from the ones of the 2*H*-indene **3a**.

Thermolysis of the C_2-symmetric spirocyclopentadienes **11** and **15** may lead to four fused cyclopentadienes; *i.e.*, the C_2-symmetric 2*H*-indene **a**, and the C_1-symmetric 1*H*-indene **b** (identical to **c**), and two C_1-symmetric 4*H*-indenes (only the *trans*-isomer **d** is shown in *Scheme 1*). Thus, the structures of **12a** and **16a** (C_2-symmetric), **12b** and **16b** (C_1-symmetric, 2 olefinic H and 1 allylic CH_2), and **12d** and **16d** are easily assigned (**12d** and **16d**: C_1-symmetric, 3 olefinic H and 1 allylic CH, strong upfield shift of H–C(i); the large J(a,i) of 12.1 (**12d**) and 11.0 Hz (**16d**) indicates the *trans*-arrangement of H–C(a) and H–C(i)). The ^{1}H-NMR spectra of **12a**/**b**/**d** and **16a**/**b**/**d** (*Table 1*) and the ^{13}C-NMR spectra of **12b** and **16b** (*Table 2*) agree well with this assignment.

The cyclohexane ring adopts a $^{f,i}B$ conformation in **3a**/**b**/**c** (as evidenced by medium $J(f_A,g)$, $J(f_B,g)$, and J(h,i); corresponding to dihedral angles of *ca.* 60°; *Table 1*), a ^gH_h conformation in **8c** (as evidenced by the large $J(f_B,g)$ of 9 Hz and the small J(h,i) of 2.4 Hz; overlap of signals prevents the analysis of **8b**), and again a ^gH_h conformation in **12d** and **16d** (evidenced by the rather small J(f,g) and J(h,i) values; *Table 1*). These conformational differences correlate with the different result of the thermolysis of **2** (→**3a**/**b**/**c** 50:25:25) and **7** (→**8b**/**c** 45:55) and the similar result of the thermolysis of **11** (→**12a**/**b**/**d** 6:86:8) and **15** (→**16a**/**b**/**d** 23:69:8).

2. *Transformation of the Annulated Cyclopentadienes into Ferrocenes.* Lithiation of the C_1-symmetric cyclopentadienes **3a**/**b**/**c** followed by treatment with $FeCl_2$ yielded 73% of a mixture of the diastereoisomeric ferrocenes **17**, **18**, and **19** in a ratio of 38:17:45 (*Scheme 2*). The statistical ratio is 25:25:50; thus, **17** is somewhat preferred. The ferrocene **17** was separated by flash chromatography, and the ferrocenes **18** and **19** by prep. HPLC. Recrystallization of **18** or **19** in hexane gave well formed yellow-red crystals.

Scheme 2



a) BuLi, THF, −60°→r.t.; $FeCl_2$, −40°→r.t.; 73%. *b*) 37% HCl, MeOH; 71% of **20**; 91% of **21**; 66% of **22**. *c*) BuLi, THF, −80°→r.t.; $FeCl_2$, −80°→r.t.; 70%. *d*) BuLi, THF, −40°→r.t.; $FeCl_2$, −60°→r.t.; 31%. *e*) BuLi, THF, −78°→−35°; $FeCl_2$, −78°→r.t.; 27%. *f*) $Hg(OAc)_2$, toluene/MeOH, r.t.; LiCl, EtOH/H_2O; 14% of **28**, 83% of **29**. *g*) As *f*); 55%. *h*) NIS, CH_2Cl_2; 93%.

The configuration of **17**–**19** was established by X-ray analysis of **18** and **19** (*Figs. 1* and *2*) and of the chloromercurio derivative **29** of **17** (see below, *Fig. 3*)[2]). The metallocene chirality is $(S,S')_m$ for **17** $(R,R')_m$ for **18**, and $(R,S')_m$ for **19**. In the solid state, the cyclohexane ring of **18** and **19** adopts a $^{[1,1]}B$ conformation as already observed for the related cyclopentadienes.

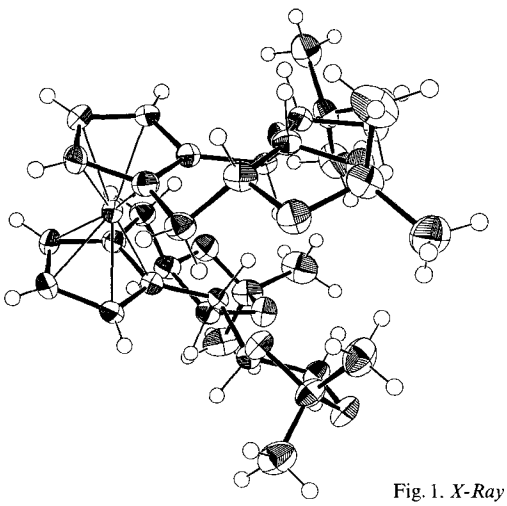


Fig. 1. *X-Ray structure of* **18**

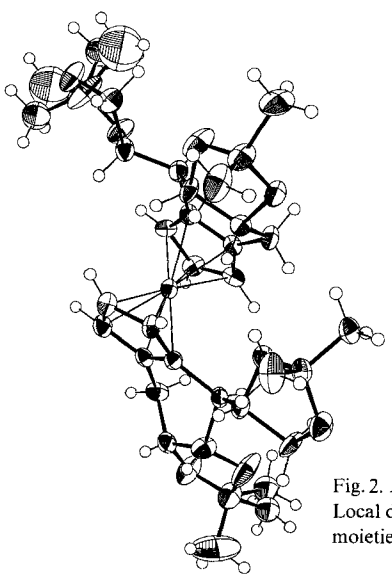


Fig. 2. *X-Ray structure of* **19**. Local disorder of two isopropylidene moieties.

[2]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England, as supplementary publication No. CCDC-10/25.

Hydrolysis of the isopropylidene acetals **17–19** with HCl in MeOH yielded the ferrocenes **20**, **21**, and **22** in 71, 91, and 66% yield, respectively. They are H_2O-soluble: 20 mg of **20** dissolve freely in 0.05 ml of H_2O, 16 mg of **21** in 0.2 ml of H_2O, and 30 mg of **22** in 0.1 ml of H_2O. Lack of material prevented the preparation of saturated solutions.

Deprotonation of the *O*-methyl-protected cyclopentadienes **8b/c** with BuLi followed by treatment with $FeCl_2$ afforded a mixture of the diastereoisomeric ferrocenes **23**, **24**, and **25** (70%; 6:42:52). In this case, the $(R,R')_m$-diastereoisomer **24** was formed to a larger extent than expected from a statistical distribution of the isomers. Their isolation was difficult; samples of **23**, **24**, and **25**, pure by NMR standards, were obtained by prep. HPLC.

The C_2-symmetry of the $(S,S')_m$-ferrocenes **17**, **20**, and **23**, and the $(R,R')_m$-isomers **18**, **21**, and **24**, and the C_1-symmetry of the $(R,S')_m$ **19**, **22**, and **25** is reflected by their NMR spectra. The three aromatic H of the ferrocenyl moieties resonate between 4.51 and 3.74 ppm (*Table 3*) and the five aromatic C as two *s* between 85.1 and 80.2 ppm, and three *d* between 72.9 and 65.8 ppm (*Exper. Part*). As in the tetrahydroindenes, the cyclohexane ring adopts a $^{f,i}B$ conformation in the isopropylidene derivatives **17–19** and a $^{g}H_h$ conformation in the methyl ethers **23–25**. This difference may be responsible for the preference of the $(S,S')_m$-isomer **17** and the $(R,R')_m$-isomer **24**, as the sterically most demanding groups of these isomers (isopropylidene in **17**; C_2 side chain in **24**) are in the least encumbered position. Broad signals and signal overlapping prevent the determination of the cyclohexane conformation of the polyols **20–22**.

Table 3. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of* **17–19** *and* **23–25**[1])

	17	**18**	**19**		**23**	**24**	**25**	
H–C(b)	4.51[a])	4.36[a])	4.32[a])	4.36[a])	4.10[a])	4.06[a])	4.11	3.97
H–C(c)	3.88	3.79	3.74	3.79	3.74	3.76	[b])	[b])
H–C(d)	4.02[a])	3.85[a])	3.90[a])	4.06[a])	3.99[a])	3.96[a])	[b])	[b])
H_A–C(f)	2.88	2.84	2.94	2.98	2.70	2.99	2.74	2.96
H_B–C(f)	2.33	2.68	2.79	2.22	2.59	2.54	2.55	2.50
H–C(g)	4.65	4.17–4.09	4.14	4.75	3.93	3.48–3.33	[b])	[b])
H–C(h)	4.24–4.18	3.86	3.78–3.74	4.26	3.71	3.66	3.69	3.62
H–C(i)	2.34	3.07	3.07	2.33	2.81	3.48–3.33	2.80–2.78	3.48–3.41
$J(f_A,f_B)$	15.4	14.4	14.3	14.4	15.0	14.5	14.7	14.7
$J(f_A,g)$	8.0	7.8	6.9	8.4	4.6	10.0	3.9	8.9
$J(f_B,g)$	6.5	8.4	8.6	7.2	8.2	5.5	8.0	5.3
J(g,h)	7.2	7.7	8.0	8.0	1.8	2.4	1.8	2.5
J(h,i)	8.7	7.7	8.0	8.0	4.4	2.4	4.4	2.5

[a]) Assignment may be interchanged. [b]) Not determined.

The Fe-atom leads to a deshielding of the neighboring H. Thus, H_A–C(f) (with the larger J(f,g)), H–C(g), and H–C(h) of **17** and H_A–C(f) (with smaller J(f,g)) and H–C(i) of **18** are deshielded (*Table 3*). This deshielding allows the unambiguous structural assignment of the methyl ethers **23** (deshielding of H_A–C(f) (J(f,g) = 4.6 Hz), H–C(g), and H–C(h)) and **24** (deshielding of H_A–C(f) (J(f,g) = 10.0 Hz) and H–C(i)). For **19** and **25**, one set of signals is similar to those of the $(S,S')_m$-isomers **17** and **23**, the other those of the $(R,R')_m$-isomers **18** and **24**. The ^{13}C-NMR spectra of the $(S,S')_m$-, $(RR')_m$-, and $(R,S')_m$-isomers show only minor differences.

Treatment of the cyclopentadienes **12a/b/d** with BuLi and $FeCl_2$ led to the expected single, C_2-symmetric ferrocene **26** (31%). Similar treatment of the cyclopentadienes

16a/b/d with BuLi and $FeCl_2$ afforded the C_2-symmetric ferrocene **27** (27%). The C_2-symmetry of the ligands implies that H–C(f) is *trans* (**26**: 2.55, **27**: 2.98–3.00 ppm) and H–C(i) *cis* (**26**: 3.14, **27**: 3.57 ppm) to the Fe-substituent.

Finally, we have synthesized a diiodoferrocene as a versatile starting material for the preparation of additionally functionalized ferrocenes. Acetoxymercuration (*cf.* [31]) of the C_2-symmetric ferrocene **17** followed by treatment with LiCl gave the C_2-symmetric 1,1′-bis(chloromercurio)ferrocene **29** in 83% yield besides 14% of the mono(chloromercurio)ferrocene **28**, both as yellow crystals. Recrystallization of **29** in toluene afforded yellow-red crystals. The configuration of **29** (ferrocene chirality $(S,S')_m$) was established by X-ray analysis (*Fig. 3*), and the one of the mono(chloromercurio)ferrocene **28** ($(S,S')_m$) by its transformation into **29** in 55% yield upon acetoxymercuration and treatment with LiCl. The C_2-symmetric 1,1′-diiodoferrocene **30** was obtained in 93% yield by the reaction of the bis(chloromercurio)ferrocene **29** with *N*-iodosuccinimide (NIS).

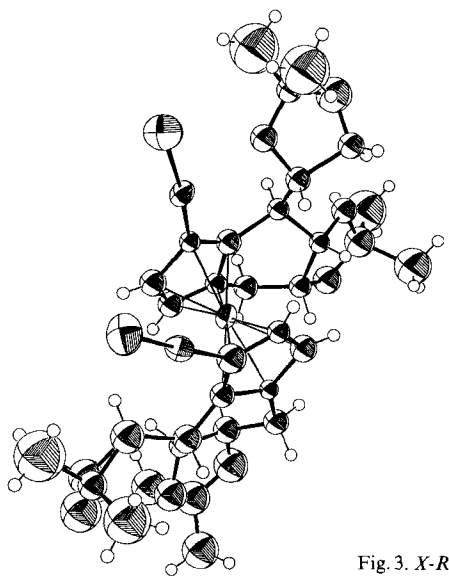


Fig. 3. *X-Ray structure of* **29**

The chloromercurio substituents of **28** and **29** are evidenced by the expected distribution of isotope of the M^+ peaks in the mass spectra: 876, 875, 874, 873, 872, and 871 (45, 44, 100, 63, 76, and 46, resp.) for **28** and 1115, 1114, 1113, 1112, 1111, 1110, 1109, 1108, 1107, 1106, 1105, and 1104 (15, 18, 48, 40, 84, 78, 77, 100, 66, 43, 28, and 14, resp.) for **29**. Iodination is confirmed by the upfield shift to 47.28 ppm of the I-substituted ferrocene C-atom in the ^{13}C-NMR spectrum of C_2-symmetric **30**.

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Experimental Part

General. Solvents were freshly distilled: THF and toluene from Na and benzophenone, MeOH and CH_2Cl_2 from CaH_2. All reactions were performed under N_2. Normal workup means distribution of the crude between CH_2Cl_2 and sat. aq. $NaHCO_3$ soln., drying of the org. layer ($MgSO_4$), and evaporation *i.v.* at or below 40° in a rotary evaporator. Anal. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by treatment with an aq. soln. of H_2SO_4 (10%), $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (5%), and $Ce(SO_4)_2\cdot 4\,H_2O$ (0.1%) followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). High-performance liquid chromatography (HPLC): anal. *Spherisorb* silica gel (5 μm, 250 × 4.6 mm column), *Nucleosil 5 CN* (5 μm, 250 × 4.0 mm column), UV detection (254 nm), 2 ml/min; prep. *Spherisorb* silica gel (5 μm, 250 × 20 mm column), *Nucleosil 5 CN* (5 μm, 250 × 21 mm column), 16 ml/min. M.p.: uncorrected. Optical rotations: 1-dm cell at 25° at 589 nm. IR Spectra: in $CHCl_3$ or KBr. ^{1}H- and ^{13}C-NMR Spectra: at 200, 300 (^{1}H), and at 75 MHz (^{13}C); chemical shifts δ in ppm rel. to $SiMe_4$, coupling constants J in Hz; ^{1}H-assignments were corroborated by selective homonuclear decoupling experiments. Mass spectra: EI at 70 V or FAB.

*(3a*S,*4*S,*6a*R,*4″*S*)-4-(2″,2″-Dimethyl-1″,3″-dioxolan-4″-yl)-3a,4,6,6a-tetrahydro-2,2-dimethylspiro[5*H*-cyclopenta-1,3-dioxole-5,1′-cyclopenta-2′,4′-diene]* (**2**). CpNa in THF (2M, 1.46 ml, 2.92 mmol) was added dropwise to a suspension of NaH (60% in mineral oil; washed with 3 × 2 ml of pentane; 117 mg, 2.93 mmol) in dry THF (1 ml). A soln. of **1** [25] (344 mg, 0.82 mmol) in dry THF (3 ml) was added at 0° to the precooled mixture *via* cannula, followed by addition of hexamethylphosphoric triamide (HMPA; 1.0 ml). The resulting slurry was stirred at r.t. for 14 h and then treated with sat. aq. NH_4Cl soln. (5 ml). Normal workup gave **2**/**3a** 13:1. FC (hexane/AcOEt 93:7) afforded **3a** (12 mg, 5%) as a pale yellow oil and **2** (151 mg, 63%) as a white solid, both slowly decomposing at r.t. R_f (hexane/AcOEt 93:7) 0.17 (**3a**), 0.13 (**2**). *Data of* **2**: M.p. 34.5–36.5°. $[\alpha]_D^{25} = +11.7$ ($c = 1.115$, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2936*s*, 1456*m*, 1382*s*, 1373*s*, 1159*s*, 1129*w*, 1057*s*, 966*w*, 853*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.52–6.47 (*m*, 1 olef. H); 6.34–6.30 (*m*, 1 olef. H); 6.27–6.22 (*m*, 2 olef. H); 4.80 (*td*, $J = 6.8$, 5.0, H–C(6a)); 4.63 (*dd*, $J = 6.8$, 5.0, H–C(3a)); 3.93–3.85 (*m*, H–C(4″), H_A–C(5″)); 3.64 (*dd*, $J = 10.5$, 9.6, H_B–C(5″)); 2.58 (*t*, $J = 5.3$, H–C(4)); 2.04 (*dd*, $J = 13.3$, 5.0, H_A–C(6)); 1.93 (*dd*, $J = 13.3$, 6.5, H_B–C(6)); 1.58 (*s*, Me); 1.40 (*s*, Me); 1.36 (*s*, Me); 1.27 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.03 (*d*); 138.12 (*d*); 130.70 (*d*); 128.36 (*d*); 112.46 (*s*); 108.59 (*s*); 83.37 (*d*); 80.18 (*d*); 75.86 (*d*); 67.29 (*t*); 65.01 (*s*); 52.66 (*d*); 39.03 (*t*); 27.06 (*q*); 26.70 (*q*); 25.25 (*q*); 24.53 (*q*). EI-MS: 292 (4, M^+), 277 (70, $[M - Me]^+$), 234 (6), 219 (29), 176 (19), 159 (26), 147 (20), 131 (39), 117 (34), 101 (41), 91 (34), 78 (21), 69 (12), 59 (27), 43 (100). Anal. calc. for $C_{17}H_{24}O_4$ (292.38): C 69.84, H 8.27; found: C 69.87, H 8.21.

Thermolysis of **2**. A soln. of **2** (1.375 g, 4.7 mmol) in toluene (200 ml) was degassed in an autoclave, heated to 240° for 4 h, cooled to r.t., and evaporated at r.t. FC (hexane/AcOEt 93:7) gave **3a**/**b**/**c** 2:1:1 (71%, 973 mg) as a pale yellow oil, slowly decomposing at r.t. A second FC afforded pure **3a**. Prep. HPLC (silica gel, hexane/AcOEt 92:8) gave pure **3b**, **3c**, and **3a** as colorless oils. A $CDCl_3$ soln. of pure **3a**, **3b**, or **3c** isomerized within several days to a mixture **3a**/**b**/**c**.

*(3a*S,*4*S,*8a*R,*4′*S*)-4-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-3a,6,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-d]-1,3-dioxole* (**3a**): R_f (hexane/AcOEt 93:7) 0.17. t_R (hexane/AcOEt 92:8) 25.8 min. $[\alpha]_D^{25} = -15.5$ ($c = 1.12$, $CHCl_3$). IR ($CHCl_3$): 3008*s*, 2985*s*, 2933*w*, 2890*m*, 1456*m*, 1380*s*, 1370*s*, 1160*s*, 1060*s*, 990*w*, 970*w*, 930*w*, 905*m*, 890*m*, 855*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.28 (br. *s*, $w_{1/2} = 5$, H–C(7)); 6.07 (br. *s*, $w_{1/2} = 5$, H–C(5)); 4.37 (*td*, $J = 7.5$, 5.9, H–C(8a)); 4.35 (*td*, $J \approx 8.0$, 6.3, H–C(4′)); 4.14 (*dd*, $J = 8.3$, 6.1, H_A–C(5′)); 4.12 (*t*, $J = 7.1$, H–C(3a)); 3.85 (*t*, $J = 8.3$, H_B–C(5′)); 3.04 (br. *d*, $J \approx 24$, H_A–C(6)); 3.02–2.94 (*m*, H_A–C(8)); 2.95 (br. *d*, $J \approx 24$, H_B–C(6)); 2.79 (*tt*, $J \approx 7.0$, 2.1, H–C(4)); 2.54 (*ddt*, $J = 14.4$, 7.5, 2.2, H_B–C(8)); 1.43 (*s*, Me); 1.40 (*s*, Me); 1.36 (*s*, Me); 1.33 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.86 (*s*); 141.31 (*s*); 127.96 (*d*); 125.57 (*d*); 108.73 (*s*); 108.36 (*s*); 77.08 (*d*); 76.57 (*d*); 74.32 (*d*); 68.04 (*t*); 43.35 (*d*); 41.30 (*t*); 29.52 (*t*); 27.15 (*q*); 26.34 (*q*); 25.68 (*q*); 24.41 (*q*).

*(3a*S,*4*S,*8a*R,*4′*S*)-4-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-d]-1,3-dioxole* (**3b**): R_f (hexane/AcOEt 93:7) 0.10. t_R (hexane/AcOEt 92:8) 37.0 min. $[\alpha]_D^{25} = -23.6$ ($c = 0.983$, $CHCl_3$). IR ($CHCl_3$): 3008*s*, 2990*s*, 2936*m*, 1602*w*, 1456*m*, 1382*s*, 1372*s*, 1157*s*, 1055*s*, 967*w*, 950*w*, 895*w*, 854*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.35 (br. *s*, H–C(6), H–C(7)); 4.46 (*td*, $J = 6.2$, 4.0, H–C(8a)); 4.23 (*q*, $J \approx 7.0$, H–C(4′)); 4.16 (*dd*, $J = 5.9$, 4.1, H–C(3a)); 4.16 (*dd*, $J = 8.3$, 6.4, H_A–C(5′)); 3.75 (*dd*, $J = 8.4$, 7.2, H_B–C(5′)); 3.11 (br. *d*, $J = 24$, H_A–C(5)); 3.00 (br. *d*, $J = 24$, H_B–C(5)); 2.87–2.80 (*m*, H–C(4)); 2.78 (br. *dd*, $J = 17.4$, 6.6, H_A–C(8)); 2.55 (br. *d*, $J = 17.4$, H_B–C(8)); 1.41 (*s*, Me); 1.40 (*s*, Me); 1.37 (*s*, 2 Me).

*(3a*S,*4*S,*8a*R,*4′*S*)-4-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-3a,7,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-d]-1,3-dioxole* (**3c**): R_f (hexane/AcOEt 93:7) 0.10. t_R (hexane/AcOEt 92:8) 41.2 min. $[\alpha]_D^{25} = -30.1$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3008*s*, 2980*s*, 2936*m*, 2901*m*, 1602*w*, 1456*w*, 1382*s*, 1372*s*, 1163*s*, 1053*s*, 968*w*, 948*w*, 869*m*, 849*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.53 (br. *d*, $J = 5.4$, H–C(5)); 6.29 (br. *d*, $J = 5.4$, H–C(6)); 4.49 (*td*, $J = 6.3$,

3.7, H–C(8a)); 4.34 (*td*, J = 7.4, 6.2, H–C(4′)); 4.26 (*dd*, J = 6.2, 3.6, H–C(3a)); 4.04 (*dd*, J = 8.4, 6.4 H_A–C(5′)); 3.70 (*dd*, J = 8.3, 7.7, H_B–C(5′)); 2.95 (br. *d*, J = 22, H_A–C(7)); 2.88 (br. *d*, J = 22, H_B–C(7)); 2.85–2.81 (*m*, H–C(4)); 2.82 (*dd*, J = 17.4, 6.5, H_A–C(8)); 2.56 (br. *d*, J = 17.4, H_B–C(8)); 1.39 (*s*, Me); 1.36 (*s*, 2 Me); 1.35 (*s*, Me).

Data of **3a**/**b**/**c**: EI-MS: 292 (0.2, M^+), 277 (1, $[M - Me]^+$), 159 (4), 131 (3), 115 (3), 101 (100), 91 (7), 43 (8). Anal. calc. for $C_{17}H_{24}O_4$ (292.38): C 69.84, H 8.27; found: C 69.87, H 8.06.

*1,2,4,5-Tetra-*O*-methyl-*D*-mannitol* (**5**). A soln. of **4** [27] (1.076 g, 4.555 mmol) in EtOH (5 ml) was added to a soln. of $NaBH_4$ (500 mg, 13.22 mmol) in EtOH (25 ml) at r.t. The mixture was stirred for 3 h, treated with MeOH (20 ml), stirred for 1 h, and evaporated. This procedure was repeated 3 times. FC (CH_2Cl_2/MeOH 9:1) afforded **5** (906 mg, 84%). White microcrystalline powder. R_f (CH_2Cl_2/MeOH 9:1) 0.56. M.p. 30–31.5°. $[\alpha]_D^{25} = -11.4$ (c = 1.06, $CHCl_3$). IR ($CHCl_3$): 3556*m* (br.), 3008*s*, 2936*s*, 2897*m*, 2831*m*, 1711*m*, 1463*m*, 1389*w*, 1343*w*, 1272*w*, 1108*s*, 1052*m*, 934*w*, 909*w*, 860*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.88 (br. *dt*, $J \approx$ 11.8, 4.2, addn. of $D_2O \rightarrow$ *dd*, J = 11.8, 4.6, H_A–C(6)); 3.75 (*dd*, J = 10.4, 3.2, H_A–C(1)); 3.76–3.65 (*m*, addn. of $D_2O \rightarrow$ 3.73 (*dd*, J = 8.7, 1.3, H–C(3)), 3.68 (*dd*, J = 11.8, 4.0, H_B–C(6)); 3.64 (*dd*, J = 6.4, 1.5, H–C(4)); 3.63 (*dd*, J = 10.6, 4.2, H_B–C(1)); 3.54 (*s*, Me); 3.46 (*s*, 2 Me); 3.48–3.42 (*m*, H–C(5)); 3.41 (*s*, Me); 3.32 (*dt*, J = 8.6, 3.5, H–C(2)); 2.83 (br. *d*, J = 7.8, exchange with D_2O, HO–C(3)); 2.39 (br. *dd*, J = 7.4, 4.4, exchange with D_2O, HO–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 81.65 (*d*); 79.52 (*d*); 77.56 (*d*); 71.09 (*t*); 69.98 (*d*); 59.98 (*q*); 59.85 (*t*); 59.19 (*q*); 58.08 (*q*); 57.32 (*q*). EI-MS: 239 (0.7, $[M + 1]^+$), 207 (1), 189 (1), 179 (3), 163 (8), 145 (8), 131 (44), 119 (25), 101 (34), 89 (100), 75 (24), 59 (24), 45 (19). Anal. calc. for $C_{10}H_{22}O_6$ (238.28): C 50.41, H 9.31; found: C 50.44, H 9.40.

*1,2,4,5-Tetra-*O*-methyl-3,6-bis-*O*-(methylsulfonyl)-*D*-mannitol* (**6**). A cooled (0°) soln. of **5** (344 mg, 1.44 mmol) and Et_3N (0.80 ml, 5.77 mmol) in dry CH_2Cl_2 (5 ml) was treated with MsCl (0.44 ml, 5.67 mmol), stirred for 1 h at 0°, and treated with sat. aq. $NaHCO_3$ soln. (5 ml). Normal workup afforded **6** (569 mg, 99%) as an oil. R_f ($CHCl_3$/MeOH 95:5) 0.62. $[\alpha]_D^{25} = +21.1$ (c = 1.05, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2938*w*, 2836*w*, 1711*w*, 1462*w*, 1414*w*, 1356*s*, 1175*s*, 1113*s*, 1015*w*, 958*m*, 911*m*, 869*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.03 (*t*, $J \approx$ 4.3, H–C(4)); 4.59 (*dd*, J = 11.4, 2.9, H_A–C(6)); 4.29 (*dd*, J = 11.4, 3.6, H_B–C(6)); 3.69 (*dd*, J = 10.3, 4.0, H_A–C(1)); 3.63 (*dd*, J = 7.0, 3.9, H–C(4)); 3.60–3.54 (*m*, H–C(2), H–C(5)); 3.52 (*s*, Me); 3.49 (*dd*, J = 10.3, 4.8, H_B–C(1)); 3.45 (*s*, Me); 3.43 (*s*, Me); 3.37 (*s*, Me); 3.09 (*s*, Ms); 3.06 (*s*, Ms). ^{13}C-NMR (75 MHz, $CDCl_3$): 79.93 (*d*); 78.95 (*d*); 78.12 (*d*); 77.86 (*d*); 70.32 (*t*); 66.67 (*t*); 60.99 (*q*); 59.06 (*q*); 57.51 (*q*); 57.35 (*q*); 38.75 (*q*); 37.55 (*q*). EI-MS: 395 (0.3, $[M + 1]^+$), 363 (1), 317 (1), 241 (1), 235 (1), 221 (2), 209 (7), 197 (10), 165 (15), 153 (6), 113 (31), 101 (100), 89 (80), 75 (18), 59 (21), 45 (19). Anal. calc. for $C_{12}H_{26}O_{10}S_2$ (394.46): C 36.54, H 6.64; found: C 36.69, H 6.50.

*(6*S*,7*S*,8*R*,1′*S*)-6-(1′,2′-Dimethoxyethyl)-7,8-dimethoxyspiro[4.4]nona-1,3-diene* (**7**). A suspension of NaH (60%, washed twice with pentane prior to use; 200 mg, 5.0 mmol) and 2M CpNa (2.20 ml, 4.40 mmol) in THF (5 ml) was treated at −80° with a soln. of **6** (569 mg, 1.44 mmol) in dry THF (4 ml), allowed to warm to r.t. during 1 h, stirred for 3 h, and treated with H_2O (10 ml). Normal workup and FC (hexane/AcOEt 85:15) afforded **7** (137 mg, 36%), **7**/**8b**/**8c** (15 mg, 4%), and **8b**/**c** 45:55 (162 mg, 42%), all as pale-yellow oils. *Data of* **7**: R_f (hexane/AcOEt 8:2) 0.25. $[\alpha]_D^{25} = -4.6$ (c = 1.06, $CHCl_3$). IR ($CHCl_3$): 3007*s*, 2930*m*, 2830*m*, 1516*w*, 1450*m*, 1370*m*, 1124*s*, 1083*s*, 1009*w*, 977*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.44–6.36 (*m*, H–C(2), H–C(3)); 6.16 (*dt*, J = 5.2, 1.7), 6.12 (*dt*, J = 5.2, 1.7, H–C(1), H–C(4)); 3.93 (*q*, $J \approx$ 4.3, H–C(8)); 3.78 (*dd*, J = 9.4, 4.6, H–C(7)); 3.49 (*s*, Me); 3.37 (*s*, Me); 3.36 (*s*, Me); 3.41–3.33 (*m*, H–C(1′)); 3.21 (*s*, Me); 3.24 (*dd*, J = 10.0, 6.9, H_A–C(2′)); 3.05 (*dd*, J = 10.0, 4.5, H_B–C(2′)); 2.66 (*dd*, J = 9.3, 4.0, H–C(6)); 1.86 (*dd*, J = 13.0, 3.8, H_A–C(9)); 1.80 (*dd*, J = 13.0, 4.4, H_B–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.72 (*d*); 142.78 (*d*); 127.99 (*d*); 126.94 (*d*); 83.78 (*d*); 80.01 (*d*); 78.89 (*d*); 73.82 (*t*); 59.30 (*q*); 59.13 (*s*); 58.63 (*q*); 57.77 (*q*); 56.59 (*q*); 47.85 (*d*); 34.07 (*t*). EI-MS: 268 (16, M^+), 236 (44), 223 (14), 204 (61), 191 (52), 172 (64), 165 (28), 159 (62), 145 (100), 135 (26), 121 (34), 101 (37), 91 (22), 75 (18), 59 (8), 45 (9). Anal. calc. for $C_{15}H_{24}O_4$ (268.35): C 67.14, H 9.01; found: C 67.20, H 9.30.

Thermolysis of **7**. A soln. of **7** (126 mg, 2.13 mmol) in toluene (40 ml) was degassed in an autoclave, heated at 231° for 4 h, cooled to r.t., and evaporated. FC (hexane/AcOEt 85:15) gave **8b**/**c** 45:55 (78 mg, 62%). Samples of **8b** and **8c**, pure according to NMR, were obtained by prep. HPLC (silica gel, hexane/AcOEt 8:2). $CDCl_3$ solns. of **8b** and **8c** isomerized over several days to a mixture **8b**/**c**.

*(5*R*,6*S*,7*S*,1′*S*)-7-(1′,2′-Dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1*H*-indene* (**8b**): R_f (hexane/AcOEt 8:2) 0.13. t_R (hexane/AcOEt 8:2) 30.3 min. $[\alpha]_D^{25} = -5.8$ (c = 0.71, $CHCl_3$). IR ($CHCl_3$): 3007*s*, 2930*m*, 2896*m*, 2828*m*, 1708*w*, 1603*w*, 1456*m*, 1377*m*, 1096*s*, 1009*w*, 968*w*, 895*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.30 (br. *AB*, $J_{AB} \approx$ 6.2, H–C(2), H–C(3)); 3.69–3.62 (*m*, H–C(5), H–C(6)); 3.61–3.50 (*m*, H–C(1′), 2 H–C(2′)); 3.46 (*s*, Me); 3.45 (*s*, Me); 3.44 (*s*, Me); 3.38 (*s*, Me); 3.09 (br. *dt*, J = 23, 2.6, H_A–C(1)); 3.01–2.97 (br. *s*, $w_{1/2} \approx$ 13, H–C(7)); 2.80 (br. *dt*, J = 23, 2.6, H_B–C(1)); 2.60–2.54 (*m*, 2 H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.35 (*s*); 136.06 (*s*); 133.46 (*d*); 132.26 (*d*); 81.12 (*d*); 78.52 (*d*); 76.56 (*d*); 74.10 (*t*); 59.05 (*q*); 58.43 (*q*); 57.71 (*q*); 56.98 (*q*); 43.07 (*t*); 42.27 (*d*); 26.75 (*t*).

(4S,5S,6R,1'S)-4-(1',2'-Dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1H-indene (**8c**): R_f (hexane/AcOEt 8:2) 0.13. t_R (hexane/AcOEt 8:2) 32.6 min. $[\alpha]_D^{25} = -39.6$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 3007*s*, 2930*m*, 2898*m*, 2828*m*, 1455*m*, 1376*m*, 1099*s*, 1008*w*, 966*w*, 948*w*, 910*w*, 862*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.37 (br. *d*, $J = 5.4$, H–C(3)); 6.23 (br. *d*, $J = 5.4$, H–C(2)); 3.69 (*t*, $J \approx 2.4$, H–C(5)); 3.61 (*ddd*, $J = 8.6, 5.9, 2.2$, H–C(6)); 3.51–3.45 (*m*, H–C(1'), 2 H–C(2')); 3.45 (*s*, Me); 3.43 (*s*, Me); 3.41 (*s*, Me); 3.38 (*s*, Me); 3.04–2.95 (br. *s*, $w_{1/2} = 10$, H–C(4)); 2.87 (br. *s*, 2 H–C(1)); 2.64 (*dd*, $J = 17.0, 5.8$, H_A–C(7)); 2.52 (*dd*, $J = 17.0, 9.0$, H_B–C(7)). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.07 (*s*); 135.48 (*s*); 133.73 (*d*); 130.79 (*d*); 81.56 (*d*); 78.08 (*d*); 77.27 (*d*); 73.39 (*t*); 59.03 (*q*); 58.38 (*q*); 57.83 (*q*); 56.70 (*q*); 43.08 (*t*); 41.29 (*d*); 27.19 (*t*).

8b/**c**: EI-MS: 268 (3, $M^{+\cdot}$), 256 (2), 236 (24), 220 (7), 204 (23), 191 (28), 172 (32), 159 (64), 147 (100), 135 (31), 117 (18), 103 (14), 91 (22), 75 (13), 59 (15), 45 (24). Anal. calc. for $C_{15}H_{24}O_4$ (268.35): C 67.14, H 9.01; found: C 67.39, H 9.25.

(2R,4aS,5aS,8R,9aR,9bR)-4,4a,5a,6,9a,9b-Hexahydro-2,8-diphenylspiro[5H-cyclopenta[2,1-d:3,4-d']bis-[1,3]dioxin-5,1'-cyclopenta-2',4'-diene] (**11**). A suspension of NaH (14 mg, 0.35 mmol) and 2M CpNa (0.175 ml, 0.35 mmol) in THF (2 ml) was treated at –15° with a soln. of **10** [29] (60 mg, 0.096 mmol) in THF (2 ml) and HMPA (0.2 ml), stirred at r.t. for 48 h, and treated with sat. aq. $NaHCO_3$ soln. (5 ml). Normal workup and FC (hexane/AcOEt 88:12) gave **11** (10 mg, 27%). White powder. R_f (hexane/Et_2O 9:1) 0.34. M.p. 167.5–169°. $[\alpha]_D^{25} = +93.0$ ($c = 0.92$, $CHCl_3$). IR ($CHCl_3$): 3071*w*, 3008*m*, 2971*w*, 2905*w*, 2855*m*, 1520*w*, 1498*w*, 1454*s*, 1394*s*, 1374*m*, 1352*w*, 1296*s*, 1135*s*, 1103*w*, 1090*m*, 1050*s*, 1028*w*, 991*s*, 912*w*, 891*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.51 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.78 (*d*, $J = 6.5$, H–C(2')); 6.29 (*d*, $J = 6.5$, H–C(1')); 5.53 (*s*, H–C(2)); 4.55 (*d*, $J = 3.1$, H–C(9b)); 4.04 (*dd*, $J = 12.1, 3.5$, H_A–C(4)); 3.64 (*d*, $J = 12.1$, H_B–C(4)); 2.91 (*t*, $J = 3.4$, H–C(4a)). ^{13}C-NMR (75 MHz, $CDCl_3$): 144.00 (2*d*); 138.40 (2*s*); 129.28 (2*d*); 129.04 (2*d*); 128.37 (4*d*); 126.18 (4*d*); 100.29 (2*d*); 82.23 (2*d*); 66.20 (2*t*); 63.58 (*s*); 40.53 (2*d*). EI-MS: 388 (3.9, $M^{+\cdot}$), 297 (3), 282 (8), 191 (8), 176 (8), 160 (4), 146 (20), 129 (16), 117 (61), 105 (68), 91 (100), 77 (76), 69 (45), 51 (27), 43 (28). Anal. calc. for $C_{25}H_{24}O_4$ (388.46): C 77.30, H 6.23; found: C 77.06, H 6.18.

Thermolysis of **11**. A soln. of **11** (523 mg, 1.346 mmol) in toluene (190 ml) was degassed in an autoclave, heated at 217° for 16 h, cooled to r.t., and evaporated. FC (hexane/Et_2O 9:1) gave **12d** (24 mg) as an oil and **12a**/**b** 7:93 (275 mg) as white crystals in a total yield of 57% (**12b**/**d**/**a** 86:8:6). Isomer **12d** isomerized over several hours to **12a**/**b**/**d**. Attempts to separate **12a** and **12b** by prep. HPLC failed.

(2R,4aS,7bS,10R,11aR,11bR)-4a,6,7b,8,11a,11b-Hexahydro-2,10-diphenyl-4H-indeno[5,4-d:6,7-d']bis-[1,3]dioxin/(2R,4aS,7bS,10R,11aR,11bR)-4a,5,7b,8,11a,11b-Hexahydro-2,10-diphenyl-4H-indeno[5,4-d:6,7-d']bis[1,3]dioxin (**12a**/**b** 7:93): R_f (hexane/Et_2O 9:1) 0.13. M.p. 165.5–168.5°. $[\alpha]_D^{25} = +37.4$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3069*w*, 3008*m*, 2977*w*, 2878*m*, 1602*w*, 1498*w*, 1456*m*, 1389*m*, 1330*w*, 1314*w*, 1134*s*, 1120*s*, 1101*w*, 1069*s*, 1015*s*, 987*m*, 904*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): signals of **12b**: 7.43–7.33 (*m*, 10 arom. H); 6.64 (*d*, $J = 5.4$, H–C(7)); 6.46 (*dd*, $J = 5.4, 1.1$, H–C(6)); 5.63, 5.625 (2*s*, H–C(2), H–C(10)); 4.66, 4.55 (2*dd*, each $J = 11.8, 1.1$, H_A–C(4), H_A–C(8)); 4.51–4.44 (*m*, H–C(11a), H–C(11b)); 4.233 (*dd*, $J = 11.8, 3.2$), 4.228 (*dd*, $J = 11.7, 2.8$, H_B–C(4), H_B–C(8)); 3.25 (br. *dquint.*, $J \approx 23, 1.5$, H_A–C(5)); 3.03 (br. *d*, $J \approx 23$, H_B–C(5)); 2.78 (br. *s*, $w_{1/2} = 8$), 2.69 (br. *s*, $w_{1/2} = 10$, H–C(4a), H–C(7b)); signals of **12a**: 6.37 (br. *q*, $J = 1.75$, H–C(5)); 5.65 (*s*, H–C(2)); 4.29 (br. *d*, $J = 1.8$, H–C(11b)); 3.12–3.08 (br. *s*, H–C(6)); 2.88–2.83 (br. *s*, H–C(4a)). ^{13}C-NMR (75 MHz, $CDCl_3$; only signals of **12b** listed): 138.35 (3*s*); 137.77 (*s*); 131.56 (*d*); 131.35 (*d*); 128.95 (*d*); 128.86 (*d*); 128.20 (2*d*); 128.15 (2*d*); 126.14 (4*d*); 101.07 (*d*); 100.91 (*d*); 75.09 (*d*); 74.73 (*d*); 70.11 (*t*); 69.16 (*t*); 41.21 (*t*); 32.41 (*d*); 31.38 (*d*).

(2R,4aS,4bS,7bS,10R,11aR,11bR)-4a,4b,7b,8,11a,11b-Hexahydro-2,10-diphenyl-4H-indeno[5,4-d:6,7-d']bis[1,3]dioxin (**12d**): R_f (hexane/Et_2O 9:1) 0.23. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.56–7.29 (*m*, 10 arom. H); 6.62 (*dt*, $J = 5.4, 1.4$, H–C(6)); 6.57 (*dd*, $J = 5.4, 0.9$, H–C(7)); 6.48 (*t*, $J = 1.4$, H–C(5)); 5.69, 5.57 (2*s*, H–C(2), H–C(10)); 4.71, 4.39 (2 br. *d*, each $J = 12.4$, H_A–C(4), H_A–C(8)); 4.42 (*t*, $J \approx 2.8$), 4.21 (*t*, $J \approx 2.8$, H–C(11a), H–C(11b)); 4.19 (*dd*, $J = 12.0, 2.8$), 4.18 (*dd*, $J = 12.2, 2.5$, H_B–C(4), H_B–C(8)); 3.71 (br. *d*, $J = 12.1$, H–C(4b)); 2.80 (br. *s*, H–C(7b)); 1.42 (br. *d*, $J = 12.1$, H–C(4a)).

Data of **12a**/**b**/**d**: EI-MS: 388 (5, $M^{+\cdot}$), 282 (3), 264 (1), 253 (3), 252 (14), 206 (3), 176 (4), 158 (3), 146 (25), 130 (47), 116 (100), 105 (44), 91 (32), 77 (41), 51 (11). Anal. calc. for $C_{25}H_{24}O_4$ (388.46): C 77.30, H 6.23; found: C 77.05, H 6.25.

1,3,4,6-Tetra-O-benzyl-2,5-bis(methylsulfonyl)-D-mannitol (**14**) [30]. A cooled (0°) soln. of **13** (3.142 g, 5.79 mmol) in dry CH_2Cl (60 ml) was treated with Et_3N (2.40 ml, 17.22 mmol) and MsCl (1.40 ml, 18.03 mmol), stirred at 0° for 30 min, at r.t. for 30 min, and treated with sat. aq. $NaHCO_3$ soln. (50 ml). Normal workup and FC (hexane/AcOEt 8:2) gave **14** (3.802 g, 94%). Oil. R_f (hexane/AcOEt 8:2) 0.15. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.34–7.25 (*m*, 10 arom. H); 4.95 (*dt*, $J = 6.8, 3.4$, H–C(2)); 4.70 (*d*, $J = 11.8$, PhC*H*); 4.63 (*d*, $J = 11.8$, PhC*H*); 4.54 (*d*, $J = 11.8$, PhC*H*); 4.47 (*d*, $J = 11.8$, PhC*H*); 4.05–3.99 (*m*, H–C(3)); 3.90 (*dd*, $J = 11.2, 3.2$, H_A–C(1)); 3.79 (*dd*, $J = 11.2, 7.0$, H_B–C(1)); 2.94 (*s*, 2 Ms).

(6S,7R,8R,9S)-7,8-Bis(benzyloxy)-6,9-bis[(benzyloxy)methyl]spiro[4.4]nona-1,3-diene (**15**). A cooled (0°) soln. of **14** (1.956 mg, 2.80 mmol) in dry THF (60 ml) was degassed, treated with HMPA (8.0 ml) and 2M CpNa in THF (4.60 ml, 9.20 mmol), and stirred at r.t. for 1 h and at 60° for 4 d. Normal workup and FC (hexane/AcOEt 95:5) gave **15** (638 mg, 40%), **15**/**16a**/**16b**/**16d** (24 mg, 1.5%), and **16a**/**b**/**d** 5:90:5 (367 mg, 23%) as pale-yellow oils. *Data of* **15**: R_f (hexane/AcOEt 9:1) 0.38. $[\alpha]_D^{25} = +82.8$ ($c = 1.09$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3067*w*, 3008*s*, 2928*m*, 2865*s*, 1950*w*, 1876*w*, 1811*w*, 1730*w*, 1604*w*, 1496*s*, 1454*s*, 1392*w*, 1364*s*, 1324*w*, 1306*w*, 1111*s*, 1078*s*, 1028*s*, 976*w*, 914*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.22 (*m*, 10 arom. H); 6.28 (*d*, $J = 6.2$, H–C(2)); 6.20 (*d*, $J = 6.2$, H–C(1)); 4.63 (*d*, $J = 12.0$, PhC*H*); 4.55 (*d*, $J = 12.0$, PhC*H*); 4.54 (*d*, $J = 11.9$, PhC*H*); 4.38 (*d*, $J = 11.9$, PhC*H*); 4.22 (*d*, $J = 4.0$, H–C(7)); 3.69 (*dd*, $J = 10.5, 9.0$, CH_A–C(6)); 3.05 (*dt*, $J \approx 10.3, 4.3$, H–C(6)); 2.81 (*dd*, $J = 9.0, 4.4$, CH_B–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 142.43 (2*d*); 138.81 (2*s*); 138.63 (2*s*); 129.39 (2*d*); 128.21 (8*d*); 127.49 (4*d*); 127.32 (4*d*); 127.28 (4*d*); 81.82 (2*d*); 72.98 (2*t*); 71.96 (2*t*); 65.98 (2*t*); 62.58 (*s*); 45.82 (2*d*). EI-MS: 572 (0.05, M^+), 481 (2), 253 (3), 181 (4), 91 (100), 65 (7). Anal. calc. for $C_{39}H_{40}O_4$ (572.75): C 81.79, H 7.04; found: C 81.61, H 6.80.

Thermolysis of **15**. A soln. of **15** (391 mg, 0.684 mmol) in toluene (80 ml) was degassed in an autoclave, heated at 230° for 5 h, and evaporated. FC (hexane/AcOEt 93:7) gave **16a**/**b**/**d** 23:69:8 (251 mg, 64%). Pure samples of **16a**, **16b**, and **16d** were obtained by a second FC (hexane/AcOEt 95:5). Pure **16a**, **16b**, and **16d** isomerized over several days to **16a**/**b**/**d**.

(4S,5R,6R,7S)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-4,5,6,7-tetrahydro-2H-indene (**16a**): R_f (hexane/AcOEt 9:1) 0.30. IR ($CHCl_3$): 3066*w*, 3005*s*, 2979*s*, 2933*w*, 2873*s*, 1950*w*, 1603*w*, 1496*m*, 1454*m*, 1384*m*, 1352*w*, 1299*w*, 1152*w*, 1111*s*, 1074*w*, 1043*w*, 1028*m*, 909*m*, 843*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.20 (*m*, 10 arom. H); 6.14 (br. *d*, $J = 1.7$, H–C(1)); 4.58 (*d*, $J = 12.0$, PhC*H*); 4.52 (*d*, $J = 12.0$, PhC*H*); 4.50 (*s*, PhCH_2); 4.07 (*d*, $J = 2.8$, H–C(5)); 3.92 (*dd*, $J = 9.0, 5.5$, CH_A–C(4)); 3.77 (*t*, $J \approx 9.2$, CH_B–C(4)); 3.34–3.23 (br. *s*, $w_{1/2} = 18$, H–C(4)); 2.89 (br. *s*, $w_{1/2} = 7.5$, H–C(2)).

(4S,5R,6R,7S)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-4,5,6,7-tetrahydro-1H-indene (**16b**): R_f (hexane/AcOEt 9:1) 0.27. IR ($CHCl_3$): 3089*w*, 3066*w*, 3007*s*, 2867*s*, 1951*w*, 1877*w*, 1812*w*, 1718*w*, 1605*w*, 1496*s*, 1454*s*, 1364*s*, 1330*m*, 1098*s*, 1028*s*, 953*w*, 912*w*, 886*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.25 (*m*, 20 arom. H); 6.52 (br. *dt*, $J = 5.4, 1.5$, H–C(3)); 6.30 (br. *dd*, $J = 5.4, 0.9$, H–C(2)); 4.63–4.51 (*m*, 4 PhCH_2); 4.07–3.98 (*m*, H–C(5), H–C(6)); 3.89 (*dd*, $J = 8.9, 5.9$), 3.79 (*dd*, $J = 8.9, 6.5$, CH_A–C(4), CH_A–C(7)); 3.75 (*t*, $J = 8.9$), 3.72 (*t*, $J = 8.9$, CH_B–C(4), CH_B–C(7)); 3.26–3.15 (*m*, H–C(4), H–C(7)); 2.92 (br. *t*, $J \approx 0.9$, 2 H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.68 (2*s*); 138.52 (2*s*); 137.39 (*s*); 136.83 (*s*); 132.08 (*d*); 131.37 (*d*); 128.29 (4*d*); 128.22 (4*d*); 127.99 (4*d*); 127.57 (4*d*); 127.52 (2*d*); 127.44 (2*d*); 74.21 (*d*); 74.12 (*d*); 73.06 (2*t*); 72.88 (*t*); 72.82 (*t*); 70.10 (*t*); 69.57 (*t*); 41.66 (*t*); 37.77 (*d*); 36.68 (*d*).

(3aS,4S,5R,6R,7S)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-3a,5,6,7-tetrahydro-4H-indene (**16d**): R_f (hexane/AcOEt 9:1) 0.35. IR ($CHCl_3$): 3089*w*, 3066*w*, 3008*s*, 2921*m*, 2866*s*, 1951*w*, 1877*w*, 1812*w*, 1720*w*, 1604*m*, 1496*s*, 1454*s*, 1364*s*, 1325*w*, 1248*w*, 1101*s*, 1068*m*, 1028*s*, 911*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.18 (*m*, 20 arom. H); 6.44 (br. *dt*, $J = 5.4, 1.6$, H–C(2)); 6.38 (br. *dd*, $J = 5.4, 1.2$, H–C(3)); 6.00 (br. *t*, $J \approx 1.2$, H–C(1)); 4.57–4.41 (*m*, PhCH_2); 4.04 (*t*, $J \approx 3.6$), 3.89 (*t*, $J = 3.6$, H–C(5), H–C(6)); 3.91 (*dd*, $J = 9.0, 5.8$), 3.73 (*dd*, $J = 8.8, 5.0$, CH_A–C(4), CH_A–C(7)); 3.84 (*t*, $J = 9.0$), 3.785 (*t*, $J = 8.8$, CH_B–C(4), CH_B–C(7)); 3.30–3.21 (*m*, H–C(7)); 2.88 (*d*, $J = 11.0$, H–C(3a)); 1.91–1.78 (*m*, H–C(4)).

Data of **16a**/**b**/**d**: $[\alpha]_D^{25} = -15.6$ ($c = 1.05$, $CHCl_3$). EI-MS: 572 (0.005, M^+), 481 (0.5), 358 (1), 267 (3), 252 (4), 237 (6), 181 (6), 161 (8), 147 (10), 131 (6), 115 (2), 105 (7), 91 (100), 77 (8). Anal. calc. for $C_{39}H_{40}O_4$ (572.75): C 81.79, H 7.04; found: C 81.90, H 6.90.

Reaction of **3a**/**b**/**c** *with BuLi and* $FeCl_2$. A cooled (−60°) soln. of **3a**/**b**/**c** 2:1:1 (757 mg, 2.59 mmol) in dry degassed THF (10 ml) was treated dropwise with 1.5M BuLi in hexane (1.90 ml, 2.85 mmol), allowed to reach r.t., and stirred for 30 min at r.t. The resulting soln. was added dropwise (*via* a cannula) to a cooled (−40°) suspension of $FeCl_2$ (342 mg, 2.70 mmol) in dry degassed THF (6 ml) at −40°. The mixture was allowed to slowly reach r.t. and stirred for 12 h at r.t. Normal workup and FC (hexane/AcOEt 93:7) gave **17**/**18**/**19** 38:17:45 (605 mg, 73%) as a yellow oil. A second FC partially separated **17** as a yellow powder. Prep. HPLC (silica gel, hexane/AcOEt 92:8) afforded pure **17**, **18**, and **19** as yellow powders. Recrystallization of **18** and **19** in hexane gave well formed yellow-red crystals, suitable for X-ray analysis.

(S,S′)$_m$-Bis{(4a,5,6,7,7a-η)-(3aS,4S,8aR,4″S)-4-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4H-indeno[5,6-d]-1,3-dioxol-5-yl}iron(II) (**17**): R_f (hexane/AcOEt 9:1) 0.13. t_R (hexane/AcOEt 92:8) 66.0 min. M.p. 59.9–62°. $[\alpha]_D^{25} = -180.3$ ($c = 0.80$, $CHCl_3$). IR ($CHCl_3$): 2989*s*, 2938*m*, 2885*m*, 1602*w*, 1456*w*, 1382*s*, 1372*s*, 1248*s*, 1161*s*, 1054*s*, 967*w*, 918*w*, 890*w*, 844*m*, 514*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.65 (*q*, $J = 7.2$, H–C(8a)); 4.51 (br. *s*, 1 arom. H); 4.38 (*td*, $J = 8.7, 5.7$, H–C(4″)); 4.24–4.18 (*m*, H_A–C(5″), H–C(3a)); 4.02 (br. *s*, 1 arom. H); 3.98 (*t*, $J = 8.2$, H_B–C(5″)); 3.88 (*t*, $J = 2.4$, 1 arom. H); 2.88 (*dd*, $J = 15.4, 8.0$, H_A–C(8));

2.34 (*t*, *J* = 8.7, H–C(4)); 2.33 (*dd*, *J* = 15.4, 6.5, H_B–C(8)); 1.49 (*s*, Me); 1.47 (*s*, Me); 1.393 (*s*, Me); 1.39 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 108.44 (*s*); 108.08 (*s*); 84.16 (*s*); 81.63 (*s*); 78.92 (*d*); 76.63 (*d*); 73.83 (*d*); 68.93 (*t*); 68.13 (*d*); 66.56 (*d*); 65.87 (*d*); 41.62 (*d*); 27.94 (*t*); 27.63 (*q*); 26.80 (*q*); 26.34 (*q*); 24.96 (*q*). EI-MS: 638 (100, $M^{+\cdot}$), 231 (6), 187 (9), 171 (5), 129 (6), 115 (8), 101 (10), 58 (6), 43 (23). Anal. calc. for $C_{34}H_{46}FeO_8$ (638.58): C 63.95, H 7.26; found: C 63.87, H 7.35.

*(*R,R′*)$_m$-Bis{(4a,5,6,7,7a-η)-(3a*S*,4*S*,8a*R*,4″*S*)-4-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-*d*]-1,3-dioxol-5-yl}iron(II)* (**18**): R_f (hexane/AcOEt 9:1) 0.09. t_R (hexane/AcOEt 92:8) 79.9 min. M.p. 133.7–135°. $[\alpha]_D^{25} = +230.1$ (*c* = 0.99, $CHCl_3$). IR ($CHCl_3$): 3000*m*, 2990*s*, 2936*m*, 2904*w*, 1602*w*, 1456*w*, 1382*s*, 1372*s*, 1265*m*, 1161*s*, 1057*s*, 967*w*, 919*w*, 888*w*, 845*w*, 517*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.36 (br. *s*, 1 arom. H); 4.33 (*q*, *J* ≈ 6.6, H–C(4″)); 4.17–4.09 (*m*, H_A–C(5″), H–C(8a)); 3.97 (*t*, *J* = 8.2, H_B–C(5″)); 3.86 (*t*, *J* = 7.7, H–C(3a)); 3.85 (*dd*, *J* = 2.5, 1.0, 1 arom. H); 3.79 (*t*, *J* = 2.4, 1 arom. H); 3.07 (*t*, *J* ≈ 7.5, H–C(4)); 2.84 (*dd*, *J* = 14.4, 7.8, H_A–C(8)); 2.68 (*dd*, *J* = 14.4, 8.4, H_B–C(8)); 1.54 (*s*, Me); 1.52 (*s*, Me); 1.44 (*s*, Me); 1.32 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.13 (*s*); 108.62 (*s*); 83.95 (*s*); 82.77 (*s*); 76.92 (*d*); 76.48 (*d*); 74.83 (*d*); 69.10 (*d*); 68.59 (*d*); 67.91 (*t*); 67.21 (*d*); 42.56 (*d*); 28.16 (*t*); 27.48 (*q*); 26.63 (*q*); 25.33 (*q*); 24.62 (*q*). EI-MS: 638 (100, $M^{+\cdot}$), 231 (6), 175 (4), 159 (6), 117 (7), 101 (38), 58 (8), 43 (35). Anal. calc. for $C_{34}H_{46}FeO_8$ (638.58): C 63.95, H 7.26; found: C 64.06, H 7.11.

*(*R,S′*)$_m$-Bis{(4a,5,6,7,7a-η)-(3a*S*,4*S*,8a*R*,4″*S*)-4-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-*d*]-1,3-dioxol-5-yl}iron(II)* (**19**): R_f (hexane/AcOEt 9:1) 0.09. t_R (hexane/AcOEt 92:8) 90.0 min. M.p. 117–118.5°. $[\alpha]_D^{25} = -44.6$ (*c* = 0.92, $CHCl_3$). IR ($CHCl_3$): 2989*m*, 2937*w*, 2886*w*, 1456*w*, 1382*s*, 1372*m*, 1161*m*, 1055*s*, 967*w*, 918*w*, 889*w*, 844*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.75 (*q*, *J* ≈ 7.2, H–C(8′a)); 4.39–4.31 (*m*, H–C(4‴)); 4.36 (br. *s*, 1 arom. H); 4.32 (br. *s*, 1 arom. H); 4.26 (*t*, *J* = 7.8, H–C(3′a)); 4.24–4.15 (*m*, H–C(4″), H_A–C(5″), H_A–C(5‴)); 4.14 (*q*, *J* = 8.0, H–C(8a)); 4.06 (br. *s*, 1 arom. H); 3.95 (*t*, *J* = 8.4, H_B–C(5‴)); 3.91 (*t*, *J* = 8.0, H_B–C(5″)); 3.90 (br. *s*, 1 arom. H); 3.79 (br. *s*, 1 arom. H); 3.78–3.74 (*m*, H–C(3a)); 3.74 (br. *s*, 1 arom. H); 3.07 (*t*, *J* = 8.4, H–C(4)); 2.98 (*dd*, *J* = 14.4, 8.4, H_A–C(8′)); 2.94 (*dd*, *J* = 14.3, 6.9, H_A–C(8)); 2.79 (*dd*, *J* = 14.4, 8.6, H_B–C(8)); 2.33 (*t*, *J* = 8.4, H–C(4′)); 2.22 (*dd*, *J* = 14.6, 7.2, H_B–C(8′)); 1.54 (*s*, 2 Me); 1.475 (*s*, Me); 1.470 (*s*, Me); 1.45 (*s*, Me); 1.42 (*s*, Me); 1.40 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.23 (*s*); 108.48 (*s*); 108.43 (*s*); 107.99 (*s*); 85.05 (*s*); 83.10 (*s*); 82.10 (*s*); 81.64 (*s*); 78.74 (*d*); 77.84 (*d*); 76.74 (*d*); 76.70 (*d*); 74.71 (*d*); 74.21 (*d*); 72.32 (*d*); 69.64 (*d*); 68.65 (*t*); 68.51 (*t*); 68.21 (*d*); 67.45 (*d*); 66.58 (*d*); 66.24 (*d*); 43.83 (*d*); 41.29 (*d*); 29.46 (*t*); 27.53 (*t*, 2*q*); 26.79 (2*q*); 26.12 (*q*); 25.81 (*q*); 24.79 (*q*); 24.60 (*q*). EI-MS: 638 (100, $M^{+\cdot}$), 231 (10), 187 (12), 171 (9), 159 (10), 131 (7), 129 (11), 115 (19), 101 (19), 91 (9), 58 (10), 43 (31), 28 (53). Anal. calc. for $C_{34}H_{46}FeO_8$ (638.58): C 63.95, H 7.26; found: C 63.98, H 7.18.

*(*S,S′*)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dihydroxyethyl)-4,5,6,7-tetrahydro-5,6-dihydroxy-1*H*-inden-1-yl]iron(II)* (**20**). A soln. of 37% HCl soln. (4 drops) and **17** (54.8 mg, 0.086 mmol) in MeOH (10 ml) was stirred at r.t. for 2 h and then evaporated. This procedure was repeated twice. FC (CH_2Cl_2/MeOH 6:4) gave **20** (29 mg, 71%) as a yellow oil (20 mg of **20** dissolved freely in 0.05 ml of H_2O). R_f (CH_2Cl_2/MeOH 6:4) 0.24. $[\alpha]_D^{25} = -24.3$ (*c* = 0.99, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): 4.38 (br. *s*, 1 H); 4.04 (br. *s*, 3 H); 3.86–3.73 (*m*, 4 H); 2.52 (br. *s*, 2 H); 2.41 (br. *s*, 2 H). ^{13}C-NMR (75 MHz, CD_3OD): 77.26 (*d*); 72.41 (*d*); 71.30 (*d*); 70.66 (*d*); 70.36 (*d*); 69.50 (*d*); 66.26 (*t*); 43.30 (*d*); 29.88 (*t*); 2*s* not detected. CI-MS (NH_3): 479 (10, $[M + 1]^+$), 478 (18), 230 (4), 213 (19), 195 (17), 177 (62), 159 (17), 145 (25), 133 (100), 117 (33), 105 (29), 91 (19), 79 (9), 55 (9).

*(*R,R′*)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dihydroxyethyl)-4,5,6,7-tetrahydro-5,6-dihydroxy-1*H*-inden-1-yl]iron(II)* (**21**). A soln. of **18** (35.9 mg, 0.056 mmol) in MeOH (10 ml) was treated with 37% HCl soln. (20 drops), stirred for 2 h at r.t., and evaporated. The residue was twice dissolved in MeOH (10 ml) and evaporated. The residue was dissolved in MeOH (10 ml), neutralized with *Amberlite IRA-93* (OH^- form) resin and filtered. Evaporation of the filtrate and FC (MeOH/AcOEt 1:1) gave **21** (25 mg, 91%) as a yellow solid (16 mg of **21** dissolved freely in 0.2 ml of H_2O). R_f (MeOH/AcOEt 1:1) 0.37. M.p. 111–113°. $[\alpha]_D^{25} = +57.6$ (*c* = 0.40, MeOH). ^{1}H-NMR (300 MHz, CD_3OD/D_2O): 4.07 (br. *s*, 1 H); 3.98 (br. *s*, 3 H); 3.93 (br. *s*, 1 H); 3.81 (br. *d*, *J* = 4.7, 1 H); 3.56–3.49 (*m*, 2 H); 3.30 (br. *s*, 1 H); 2.84 (br. *d*, *J* = 15.3, H_A–C(7)); 2.50 (br. *d*, *J* = 15.3, H_B–C(7)). ^{13}C-NMR (75 MHz, CD_3OD/D_2O): 82.32 (*s*); 82.29 (*s*); 75.26 (*d*); 73.17 (*d*); 71.53 (*d*); 70.33 (*d*); 69.35 (*d*); 68.23 (*d*); 64.73 (*t*); 42.38 (*d*); 29.50 (*t*). CI-MS (NH_3): 479 (17, $[M + 1]^+$), 478 (17, $M^{+\cdot}$), 340 (4), 234 (3), 213 (11), 195 (10), 177 (60), 159 (100), 145 (68), 133 (64), 117 (99), 91 (61), 79 (27).

*(*R,S′*)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dihydroxyethyl)-4,5,6,7-tetrahydro-5,6-dihydroxy-1*H*-inden-1-yl]iron(II)* (**22**). A soln. of **19** (89 mg, 0.14 mmol) in MeOH (5 ml) was treated with 37% HCl soln. (6 drops), stirred at r.t. for 5 h, and evaporated. The residue was dissolved in MeOH (5 ml), neutralized with *Amberlite IRA-93* resin (OH^- form), and filtered. Evaporation of the filtrate and FC (CH_2Cl_2/MeOH 1:1) gave **22** (44.3 mg, 66%) as a yellow oil (30 mg of **22** dissolved freely in 0.1 ml of H_2O). R_f (CH_2Cl_2/MeOH 6:4) 0.38. ^{1}H-NMR (200 MHz, CD_3OD): 4.58 (br. *s*, 1 H); 4.48–4.24 (*m*, 2 H); 4.17–3.98 (*m*, 2 H); 3.82 (br. *s*, 2 H); 3.65–3.58

(*m*, 1 H); 2.59 (br. *s*, 1 H); 2.41 (br. *s*, 2 H). ^{13}C-NMR (75 MHz, CD_3OD): 76.59 (*d*); 75.44 (*d*); 74.28 (*d*); 73.29 (*d*); 72.80 (*d*); 72.37 (*d*); 71.05 (*d*); 70.68 (*d*); 70.38 (*d*); 69.43 (*d*); 68.71 (*d*); 67.55 (*d*); 66.21 (*t*); 64.97 (*t*); 42.76 (*d*); 42.49 (*d*); 30.34 (*t*); 29.52 (*t*); 4*s* not detected. CI-MS (NH_3): 480 (11), 479 (37, $[M+1]^+$), 478 (70), 460 (6), 444 (4), 416 (6), 213 (12), 195 (12), 177 (43), 158 (19), 145 (28), 133 (100), 117 (48), 105 (31), 91 (28), 79 (13), 55 (10), 43 (11).

Reaction of **8b**/**c** *with BuLi and* $FeCl_2$. A cooled (−80°) soln. of **8b**/**c** 45:55 (696 mg, 2.59 mol) in dry THF (10 ml) was degassed, treated with 1.5M BuLi in hexane (2.08 ml, 3.12 mmol), allowed to reach r.t., stirred at r.t. for 30 min, and added to a cooled (−80°) suspension of $FeCl_2$ (342 mg, 2.70 mmol) in THF (5 ml). The mixture was allowed to warm to r.t. within 2 h and stirred for 46 h at r.t. Normal workup and FC (hexane/AcOEt 4:6→3:7) gave **23**/**24**/**25** 6:42:52 (538 mg, 70%) as a yellow oil. Prep. HPLC (*Nucleosil 5 CN*, hexane/AcOEt 7:3) gave pure (^{1}H-NMR) samples of **23**–**25**.

*(S,S′)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1*H*-inden-1-yl]iron(II)* (**23**). R_f (hexane/AcOEt 3:7) 0.21. t_R (hexane/AcOEt 7:3) 26.8 min. IR ($CHCl_3$): 3007*s*, 2930*s*, 2828*m*, 1602*w*, 1463*m*, 1366*w*, 1262*m*, 1103*s*, 1013*s*, 970*m*, 906*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.10 (*t*, *J* = 2.4, 1 arom. H); 3.99 (*dd*, *J* = 2.3, 1.1, 1 arom. H); 3.93 (*ddd*, *J* = 7.9, 4.7, 2.1, H–C(6)); 3.86–3.76 (*m*, H–C(1″), 2 H–C(2″)); 3.74 (*dd*, *J* = 2.1, 1.1, 1 arom. H); 3.71 (*dd*, *J* = 4.3, 1.6, H–C(5)); 3.58 (*s*, Me); 3.461 (*s*, Me); 3.459 (*s*, Me); 3.41 (*s*, Me); 2.81 (*dd*, *J* = 5.5, 4.5, H–C(4)); 2.70 (*dd*, *J* = 15.0, 4.6, H_A–C(7)); 2.59 (*dd*, *J* = 15.0, 8.2, H_B–C(7)).

*(R,R′)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1*H*-inden-1-yl]iron(II)* (**24**). R_f (hexane/AcOEt 3:7) 0.21. t_R (hexane/AcOEt 7:3) 20.2 min. $[\alpha]_D^{25} = +232.5$ (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): 3007*s*, 2930*s*, 2897*m*, 2827*m*, 1602*w*, 1453*m*, 1386*w*, 1104*s*, 1032*w*, 969*w*, 910*w*, 827*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.06 (br. *s*, 1 arom. H); 3.96 (br. *s*, 1 arom. H); 3.76 (br. *s*, 1 arom. H); 3.66 (br. *t*, *J* = 2.4, H–C(5)); 3.56 (*s*, Me); 3.48–3.33 (*m*, 5 H); 3.45 (*s*, Me); 3.42 (*s*, Me); 3.35 (*s*, Me); 2.99 (*dd*, *J* = 14.8, 10.0, H_A–C(7)); 2.54 (*dd*, *J* = 14.5, 5.5, H_B–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 82.15 (*d*); 81.85 (*s*); 81.15 (*s*); 77.70 (*d*); 77.29 (*d*); 73.18 (*t*); 71.43 (*d*); 69.77 (*d*); 67.21 (*d*); 58.66 (*q*); 57.98 (*q*); 57.15 (*q*); 56.39 (*q*); 39.81 (*d*); 24.90 (*t*).

*(R,S′)$_m$-Bis[(1,2,3,3a,7a-η)-(4*S*,5*S*,6*R*,1″*S*)-4-(1″,2″-dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1*H*-inden-1-yl]iron(II)* (**25**). R_f (hexane/AcOEt 3:7) 0.21. t_R (hexane/AcOEt 7:3) 24.0 min. $[\alpha]_D^{25} = +21.9$ (*c* = 1.05, $CHCl_3$). IR ($CHCl_3$): 3007*s*, 2930*s*, 2827*m*, 1602*w*, 1463*m*, 1365*w*, 1104*s*, 1032*w*, 1009*w*, 970*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.11 (*dd*, *J* = 2.5, 1.0, 1 arom. H); 3.97 (*dd*, *J* = 2.5, 1.0, 1 arom. H); 3.94–3.78 (*m*, 8 H); 3.69 (*dd*, *J* = 4.4, 1.4, H–C(6)); 3.62 (br. *t*, *J* ≈ 2.5, H–C(6′)); 3.58 (*s*, Me); 3.56 (*s*, Me); 3.48–3.41 (*m*, 5 H); 3.46 (*s*, Me); 3.45 (*s*, Me); 3.44 (*s*, Me); 3.43 (*s*, Me); 3.40 (*s*, Me); 3.37 (*s*, Me); 2.96 (*dd*, *J* = 14.7, 8.9, H_A–C(7′)); 2.80–2.78 (*m*, H–C(4)); 2.74 (*dd*, *J* = 14.7, 3.9, H_A–C(7)); 2.55 (*dd*, *J* = 14.5, 8.0, H_B–C(7)); 2.50 (*dd*, *J* = 14.7, 5.3, H_B–C(7′)). ^{13}C-NMR (75 MHz, $CDCl_3$): 84.44 (*s*); 82.82 (*d*); 82.01 (*s*); 81.88 (*d*); 81.50 (*s*); 80.28 (*s*); 79.14 (*d*); 78.03 (*d*); 77.50 (*d*); 77.04 (*d*); 73.29 (*t*); 73.00 (*t*); 72.84 (*d*); 70.02 (*d*); 69.27 (*d*); 67.78 (*d*); 67.48 (*d*); 66.68 (*d*); 59.06 (*q*); 59.02 (*q*); 58.42 (*q*); 57.70 (*q*); 57.33 (*q*); 57.04 (*q*); 56.90 (*q*); 56.82 (*q*); 39.67 (*d*); 38.81 (*d*); 25.60 (*t*); 25.30 (*t*).

Data of **23**/**24**/**25**: EI-MS: 590 (100, $M^{+\cdot}$), 323 (7), 229 (6), 203 (9), 172 (14), 141 (17), 115 (15), 89 (10), 59 (5). Anal. calc. for $C_{30}H_{46}FeO_8$ (590.54): C 61.02, H 7.85; found: C 60.91, H 7.98.

*Bis{(4b,5,6,7,7a-η)-(2*R*,4a*S*,7b*S*,10*R*,11a*R*,11b*R*)-4a,4b,7b,8,11a,11b-hexahydro-2,10-diphenyl-4*H*-indeno[4,5-d:6,7-d′]bis[1,3]dioxin-4b-yl}iron(II)* (**26**). A cooled (−80°) soln. of **12a**/**b**/**d** 6:86:8 (61 mg, 0.157 mmol) in dry THF (2 ml) was degassed, treated with 1.5M BuLi in hexane (0.130 ml, 0.195 mmol), allowed to warm to r.t. within 30 min, and added to a cooled (−80°) suspension of $FeCl_2$ (28.0 mg, 0.22 mmol) in dry THF (2 ml). The mixture was allowed to reach r.t. within 1 h and stirred at r.t. for 12 h. Normal workup and FC (hexane/AcOEt 88:12) gave **26** (20 mg, 31%). Yellow crystals. R_f (hexane/AcOEt 8:2) 0.23. M.p. 167–169°. $[\alpha]_D^{25} = +125.5$ (*c* = 1.13, $CHCl_3$). IR ($CHCl_3$): 3069*w*, 3008*m*, 2972*w*, 2924*w*, 2857*m*, 1498*w*, 1455*m*, 1390*s*, 1374*w*, 1351*w*, 1312*w*, 1285*w*, 1147*s*, 1109*s*, 1086*m*, 1051*m*, 1020*s*, 995*s*, 931*w*, 912*w*, 899*w*, 876*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.68–7.61 (*m*, 4 arom. H); 7.44–7.34 (*m*, 6 arom. H); 5.76 (*s*), 5.53 (*s*, H–C(2), H–C(10)); 4.67 (br. *d*, *J* = 11.5, H_A–C(8)); 4.47–4.36 (*m*, H_A–C(4), H–C(11a), H–C(11b), H_B–C(8)); 4.43 (br. *s*, 1 arom. H); 4.24 (br. *s*, 1 arom. H); 4.17 (*dd*, *J* = 11.7, 2.6, H_B–C(4)); 3.65 (br. *s*, 1 arom. H); 3.14 (br. *s*, H–C(7b)); 2.55 (*t*, *J* = 3.8, H–C(4a)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.38 (*s*); 138.15 (*s*); 128.77 (*d*); 128.49 (*d*); 128.13 (2*d*); 128.06 (2*d*); 126.11 (2*d*); 125.84 (2*d*); 101.36 (*d*); 100.75 (*d*); 83.22 (*s*); 81.11 (*s*); 76.04 (*d*); 75.27 (*d*); 72.56 (*d*); 69.81 (*t*); 69.01 (*t*); 67.76 (*d*); 65.84 (*d*); 31.55 (*d*); 28.62 (*d*). EI-MS: 830 (100, $M^{+\cdot}$), 586 (5), 443 (28), 277 (5), 199 (6), 171 (22), 129 (9), 105 (88), 77 (59).

*Bis[(1,2,3,3a,7a-η)-(4*S*,5*R*,6*R*,7*S*)-5,6-bis(benzyloxy)-4,7-bis(benzyloxymethyl)-4,5,6,7-tetrahydro-1*H*-inden-1-yl]iron(II)* (**27**). A cooled (−80°) soln. of **16a**/**b**/**d** 23:69:8 (99 mg, 0.172 mmol) in dry THF (4 ml) was degassed, treated with 1.6M BuLi in hexane (0.120 ml, 0.192 mmol), stirred at −80° for 10 min, and added to a

cooled (−80°) suspension of $FeCl_2$ (14.2 mg, 0.112 mmol) in dry THF (3 ml). The mixture was allowed to warm to r.t. within 2 h and stirred at r.t. for 24 h. Normal workup and FC (hexane/AcOEt 93:7) gave **27** (28 mg, 27%). Yellow oil. R_f (hexane/AcOEt 9:1) 0.15. $[\alpha]_D^{25} = -87.0$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 3088*w*, 3066*w*, 3008*s*, 2918*m*, 2866*s*, 1496*m*, 1454*s*, 1362*s*, 1329*w*, 1099*s*, 1071*s*, 1047*m*, 1028*m*, 928*w*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.14 (*m*, 20 arom. H); 4.59 (*s*, PhCH_2); 4.483 (*s*, PhCH_2); 4.478 (*d*, $J = 11.8$, PhC*H*); 4.41 (*s*, PhCH_2); 4.39 (*d*, $J = 11.8$, PhC*H*); 4.08 (*t*, $J = 9.0$, CH_A–C(4)); 4.02–3.98 (*m*, H–C(5)); 3.97 (br. *s*, 1 arom. H); 3.92 (*t*, $J = 4.1$, H–C(6)); 3.84 (*dd*, $J = 8.8, 5.2$, CH_B–C(4)); 3.76 (br. *s*, 2 arom. H); 3.57 (br. *s*, H–C(4)); 3.50–3.47 (*m*, CH_2–C(7)); 3.00–2.98 (*m*, H–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.74 (2*s*); 138.64 (*s*); 138.49 (*s*); 128.33 (*d*); 128.26 (5*d*); 128.12 (3*d*); 128.00 (3*d*); 127.62 (3*d*); 127.50 (*d*); 127.44 (3*d*); 127.31 (*d*); 82.13 (*s*); 82.03 (*s*); 73.60 (*d*); 73.60 (*t*); 73.43 (*d*); 73.01 (*t*); 72.78 (*t*); 72.49 (*t*); 70.93 (*t*); 69.36 (*t*); 69.14 (*d*); 68.30 (*d*); 63.61 (*d*); 35.07 (*d*); 34.53 (*d*). FAB-MS: 1199 (100, M^+), 1108 (12), 1000 (13), 892 (4), 627 (13), 91 (27).

Chloromercuration of **17**. A soln. of **17** (19.0 mg, 0.03 mmol) in dry toluene (1 ml) was treated with a soln. of $Hg(OAc)_2$ (40 mg, 0.184 mmol) in dry MeOH (1 ml), stirred at r.t. for 14 h, treated with a soln. of LiCl (40 mg, 0.94 mmol) in EtOH/H_2O 1:1 (2 ml), heated to reflux for 2 h, and cooled. After the addition of H_2O (10 ml), the mixture was extracted with toluene (3 × 20 ml). Drying the org. layer ($MgSO_4$), evaporation, and FC (hexane/AcOEt 8:2→7:3) gave **28** (4.5 mg, 14%) and **29** (27.4 mg, 83%) as yellow crystals. Recrystallization of **29** in toluene gave well formed yellow-red crystals suitable for X-ray analysis.

*(S,S′)$_m$-{(4a,5,6,7,7a-η)-(3a*S*,4*S*,8a*R*,4″*S*)-4-(2″,2″-Dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-*d*]-1,3-dioxol-5-yl}{(4′a,5′,6′,7′,7′a-η)-(3′a*S*,4′*S*,8′a*R*,4‴*S*)-5′-(chloromercurio)-4′-(2‴,2‴-dimethyl-1‴,3‴-dioxolan-4‴-yl)-3′a,5′,8′,8′a-tetrahydro-2′,2′-dimethyl-4*H*-indeno[5,6-*d*]-1′,3′-dioxol-5′-yl}iron(II)* (**28**): R_f (hexane/AcOEt 8:2) 0.22. M.p. 72–74°. $[\alpha]_D^{25} = -135.8$ ($c = 0.97$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2990*m*, 2936*m*, 1709*w*, 1602*w*, 1456*m*, 1382*s*, 1374*s*, 1158*s*, 1054*s*, 966*w*, 911*w*, 886*m*, 839*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.62 (*dd*, $J = 7.5, 4.4$), 4.57 (*dd*, $J = 7.3, 4.4$, H–C(8a), H–C(8′a)); 4.61 (*d*, $J = 2.6$, 1 arom. H); 4.40–4.32 (*m*, H–C(4″), H–C(4‴)); 4.28 (*dd*, $J = 8.9, 5.7$), 4.25 (*dd*, $J = 8.7, 5.6$, H_A–C(5″), H_A–C(5‴)); 4.20 (*t*, $J = 7.2$), 4.13 (*t*, $J = 7.2$, H–C(3a), H–C(3′a)); 4.16 (*dd*, $J = 8.7, 7.7$), 4.03 (*dd*, $J = 8.7, 7.4$, H_B–C(5″), H_B–C(5‴)); 4.15 (*d*, $J = 2.2$, 1 arom. H); 4.08 (*t*, $J = 2.4$, 1 arom. H); 3.95 (*d*, $J = 2.2$, 2 arom. H); 2.83 (*dd*, $J = 15.3, 7.4$), 2.78 (*dd*, $J = 15.9, 7.2$, H_A–C(8), H_A–C(8′)); 2.49, 2.45 (*dd*, each $J = 9.4, 7.4$, H–C(4), H–C(4′)); 2.31 (*dd*, $J = 15.0, 7.7$), 2.24 (*dd*, $J = 14.9, 7.8$, H_B–C(8), H_B–C(8′)); 1.63 (*s*, Me); 1.52 (*s*, Me); 1.473 (*s*, Me); 1.466 (*s*, Me); 1.46 (*s*, Me); 1.41 (*s*, Me); 1.39 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 110.54 (*s*); 109.16 (*s*); 108.29 (*s*); 108.18 (*s*); 85.88 (*s*); 84.91 (*s*); 84.13 (*s*); 82.71 (*s*); 81.96 (*s*); 79.50 (*d*); 79.30 (*d*); 76.24 (*d*); 76.19 (*d*); 73.97 (*d*); 73.69 (2*d*); 69.69 (*d*); 68.60 (2*t*); 67.36 (*d*); 67.05 (*d*); 66.46 (*d*); 43.16 (*d*); 41.91 (*d*); 28.06 (*t*); 28.03 (*t*); 27.58 (*q*); 27.52 (*q*); 26.89 (*q*); 26.65 (*q*); 26.51 (*q*); 26.43 (*q*); 24.88 (*q*); 24.79 (*q*). EI-MS: 876, 875, 874, 873, 872, 871 (45, 44, 100, 63, 76, 46, M^+), 638 (26), 622 (19), 564 (7), 289 (5), 231 (16), 187 (20), 131 (26), 115 (33), 101 (21), 43 (21).

*(S,S′)$_m$-Bis{(4a,5,6,7,7a-η)-(3a*S*,4*S*,8a*R*,4″*S*)-5-(chloromercurio)-4-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-2,2-dimethyl-4*H*-indeno[5,6-*d*]-1,3-dioxol-5-yl}iron(II)* (**29**): R_f (hexane/AcOEt 8:2) 0.09. M.p. 244–245° (dec.). $[\alpha]_D^{25} = -183$ ($c = 0.94$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2991*s*, 2937*m*, 1733*w*, 1602*m*, 1456*m*, 1383*s*, 1374*s*, 1154*s*, 1054*s*, 1020*w*, 966*w*, 930*w*, 887*s*, 838*s*. H-NMR (300 MHz, $CDCl_3$): 4.55 (*dt*, $J \approx 9.0, 6.9$, H–C(8a)); 4.44–4.37 (*m*, H–C(4″)); 4.35 (*d*, $J = 2.2$, 1 arom. H); 4.29 (*dd*, $J = 9.1, 6.0$, H_A–C(5″)); 4.21 (*t*, $J \approx 7.8$, H_B–C(5″)); 4.19 (*d*, $J = 2.4$, 1 arom. H); 4.16 (*t*, $J = 7.1$, H–C(3a)); 2.73 (*dd*, $J = 14.6, 6.7$, H_A–C(8)); 2.52 (*dd*, $J = 9.6, 6.9$, H–C(4)); 2.17 (*dd*, $J = 14.6, 9.2$, H_B–C(8)); 1.63 (*s*, Me); 1.47 (*s*, Me); 1.46 (*s*, Me); 1.38 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 110.62 (*s*); 108.26 (*s*); 87.12 (*s*); 84.56 (*s*); 84.47 (*s*); 79.00 (*d*); 76.05 (*d*); 74.08 (2*d*); 70.68 (*d*); 68.29 (*t*); 43.92 (*d*); 28.21 (*t*); 27.45 (*q*); 26.70 (*q*); 26.60 (*q*); 24.62 (*q*). FAB-MS: 1115, 1114, 1113, 1112, 1111, 1110, 1109, 1108, 1107, 1106, 1105, 1104 (15, 18, 48, 40, 84, 78, 77, 100, 66, 43, 28, 14, M^+), 460 (5), 307 (22), 154 (29).

Transformation of **28** *to* **29**. As described above, with **28** (43 mg, 0.0492 mmol), dry toluene (2 ml), $Hg(OAc)_2$ (27 mg, 0.085 mmol), MeOH (2 ml), LiCl (19 mg, 0.45 mmol), and EtOH/H_2O 1:1 (1 ml). Workup with H_2O (10 ml) and toluene (3 × 10 ml). FC (hexane/AcOEt 8:2) gave **29** (24 mg, 55%) and **28** (15 mg, 35%).

*(S,S′)$_m$-Bis{(4a,5,6,7,7a-η)-(3a*S*,4*S*,8a*R*,4″*S*)-4-(2″,2″-dimethyl-1″,3″-dioxolan-4″-yl)-3a,5,8,8a-tetrahydro-5-iodo-2,2-dimethyl-4*H*-indeno[5,6-*d*]-1,3-dioxol-5-yl}iron(II)* (**30**). A cooled (−10°) soln. of **29** (123 mg, 0.11 mmol) in dry $CHCl_2$ (4 ml) was treated dropwise with a soln. of NIS (100 mg, 0.444 mmol) in dry CH_2Cl_2 (4 ml), stirred for 1 h at −10°, treated with 10% aq. $NaHSO_3$ (10 ml) and 10% aq. Na_2CO_3 soln. (10 ml), and extracted with $CHCl_3$ (3 × 20 ml). Drying of the org. layer ($MgSO_4$), evaporation, and FC (hexane/AcOEt 6:4) gave **30** (92 mg, 93%). Yellow crystals. R_f (hexane/AcOEt 1:1) 0.22. M.p. 61–63°. $[\alpha]_D^{25} = +30.2$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2989*s*, 2934*m*, 1723*m*, 1602*w*, 1455*w*, 1430*w*, 1382*s*, 1373*s*, 1159*s*, 1047*s*, 969*w*, 923*w*, 909*w*, 855*m*, 829*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.50–4.44 (*m*, H–C(8a)); 4.43 (*q*, $J \approx 8.1$, H–C(4″)); 4.31 (*dd*, $J = 8.1, 6.2$, H_A–C(5″)); 4.24 (*dd*, $J = 4.4, 1.7$, H–C(3a)); 4.23 (*d*, $J = 2.2$, 1 arom. H); 4.05 (*d*, $J = 2.2$, 1 arom. H); 3.95 (*t*,

J = 8.1, H_B–C(5″)); 2.87 (*dd*, J = 8.7, 1.8, H–C(4)); 2.51 (*dd*, J = 15.3, 4.0, H_A–C(8)); 2.44 (*dd*, J = 15.3, 3.1, H_B–C(8)); 1.58 (*s*, Me); 1.49 (*s*, Me); 1.25 (*s*, Me); 1.05 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.30 (*s*); 107.92 (*s*); 87.87 (*s*); 81.00 (*d*); 81.00 (*s*); 76.31 (*d*); 75.49 (*d*); 74.51 (*d*); 72.36 (*d*); 68.54 (*t*); 47.28 (*s*); 44.18 (*d*); 28.07 (*t*); 26.62 (2*q*); 26.08 (*q*); 24.54 (*q*). ^{13}C-NMR (75 MHz, C_6D_6): 109.34 (*s*); 107.96 (*s*); 88.92 (*s*); 81.40 (*s*); 80.92 (*d*); 76.88 (*d*); 76.00 (*d*); 74.90 (*d*); 72.79 (*d*); 68.94 (*t*); 49.94 (*s*); 44.70 (*d*); 28.56 (*t*); 26.97 (*q*); 26.87 (*q*); 26.43 (*q*); 24.75 (*q*). EI-MS: 890 (100, $M^{+\cdot}$), 764 (7.7), 357 (4.3), 313 (3.1), 241 (4.4), 201 (7.2), 157 (12), 131 (22), 115 (19), 101 (21), 43 (19).

X-Ray Analysis of **18**. $C_{34}H_{46}FeO_8$ (638.56); hexagonal $P3(1)$ 21; a = 9.349 (2) Å, b = 9.349 (2) Å, c = 32.948 (6) Å; V = 2493.7 (10) Å^3; D_x = 1.276 Mg/m^3; Z = 3. Intensities were measured in the ω-scan mode on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, MoK_α, λ = 0.71073 Å) at 178 K. Of the 3585 total collected reflections, 3585 independent reflections were observed. R = 0.0347, R_w = 0.1018.

X-Ray Analysis of **19**. $C_{34}H_{46}FeO_8$ (638.56); orthorhombic $P2_12_12_1$; a = 8.933 (2) Å, b = 12.922 (4) Å, c = 28.482 (11) Å; V = 3288 (2) Å^3; D_x = 1.290 Mg/m^3; Z = 4. Intensities were measured as described for **18** at 183 K. Of the 4138 total collected reflections, 4138 independent reflections were observed. R = 0.0878, R_w = 0.2206.

X-Ray Analysis of **29**. $C_{34}H_{44}Cl_2FeHg_2O_8$ (1108.62); monoclinic $C2$; a = 30.355 (6) Å, b = 6.713 (3) Å, c = 21.222 (6) Å; V = 3845 (2) Å^3; D_x = 1.915 Mg/m^3; Z = 4. Intensities were measured as described for **18** at 293 K. Of the 3340 total collected reflections, 3312 independent reflections were observed. R = 0.0764, R_w = 0.1812. The positions of the Hg-atoms were found by the *Patterson* method, the remaining non-H-atoms were found in several steps from difference *Fourier* maps selecting carefully one part of the centrosymmetric structure (SHELX-86). The non-H-atoms were refined anisotropically with SHELXL-92.

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