

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 H₂O-soluble ferrocenes **20–22**; chloromercuration and iodination of **17** via **29** led to the C₂-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 R₂Zn [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 H₂O-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 C₁-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.

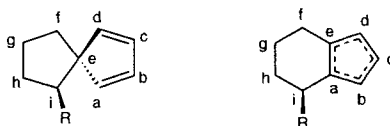
Results and Discussion. – 1. *Annulated Cyclopentadienes.* We have applied the method of *Halterman* and coworkers [1] [15] [16] [21], dialkylation of cyclopentadiene with primary 1,4-diols, to the synthesis of annulated cyclopentadienes possessing a side chain at the α -position, by alkylating cyclopentadiene 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 cyclopentadienylnsodium (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 ¹H-NMR spectrum of the crude product. Flash chromatography separated **3a** from **3b/c**; pure **3b** and **3c** were obtained by prep. HPLC.

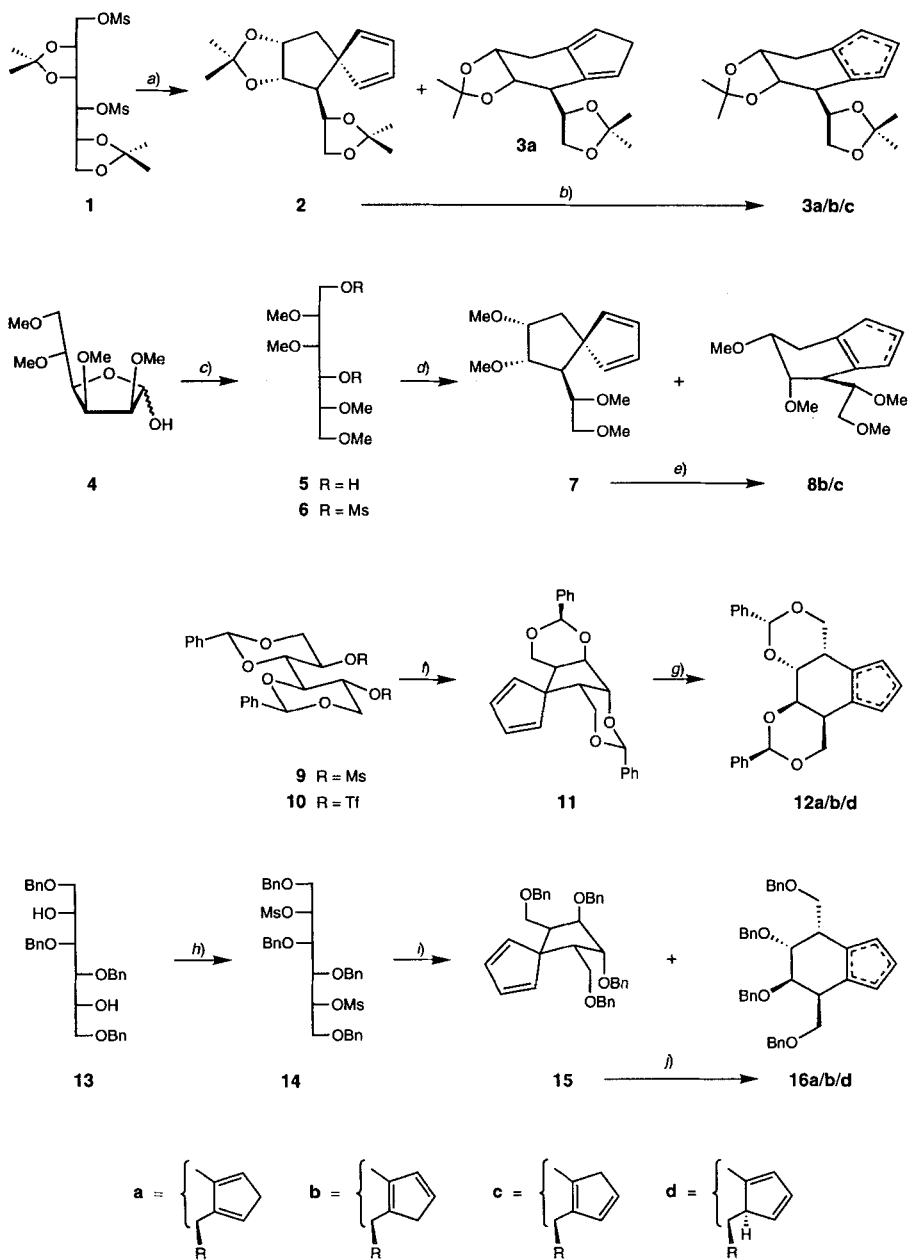
O-Isopropylidene-protected titanocenes are acid-labile [24]. For this reason, we have also prepared the *O*-methylated analogues **8** of **3**. The tetra-*O*-methyl-D-mannofuranose **4** [27] was reduced by NaBH₄ to the diol **5** (84%) and dimesylated to **6** (99%). Alkylation of **6** with CpNa and 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 ¹H-NMR spectroscopy). Pure samples of **8b** and **8c** were obtained by prep. HPLC. They isomerized in CDCl₃ 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-

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) NaBH₄, EtOH; 84% of **5**; MsCl, Et₃N, CH₂Cl₂; 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, Et₃N, CH₂Cl₂; 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 an 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 $^1\text{H-NMR}$ (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**¹⁾

	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)} $J_{\text{gem}} = 24.0$ (**3a**, **3b**), 22.0 (**3c**), and 23.0 Hz (**8b**, **12b**). Not determined for **8c**. ^{d)} $J_{\text{vic}} = 5.2$ (**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(e) 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 CH₂(f) of **2** and **7** (¹H-NMR: *dd* at 2.04 and 1.93 ppm ($J_{\text{gem}} = 13.3$ Hz; **2**) and at 1.86 and 1.80 ppm ($J_{\text{gem}} = 13$ Hz; **7**); ¹³C-NMR: *t* at 39.03 (**2**) and 34.07 ppm (**7**)), CH(i) of **2** and **7** (¹H-NMR: *t* at 2.58 ($J = 5.1$ Hz; **2**) and *dd* at 2.66 ppm ($J = 9.3, 4.0$ Hz; **7**); ¹³C-NMR: *d* at 52.66 (**2**) and 47.85 ppm (**7**)), and of CH(f) of **11** and **15** (¹H-NMR: *t* at 2.91 ($J = 3.4$ Hz; **11**) and *dt* at 3.05 ppm ($J = 10.3, 4.0$ Hz; **15**); ¹³C-NMR: *d* at 40.53 (**11**) and 45.82 ppm (**15**)) are shifted upfield.

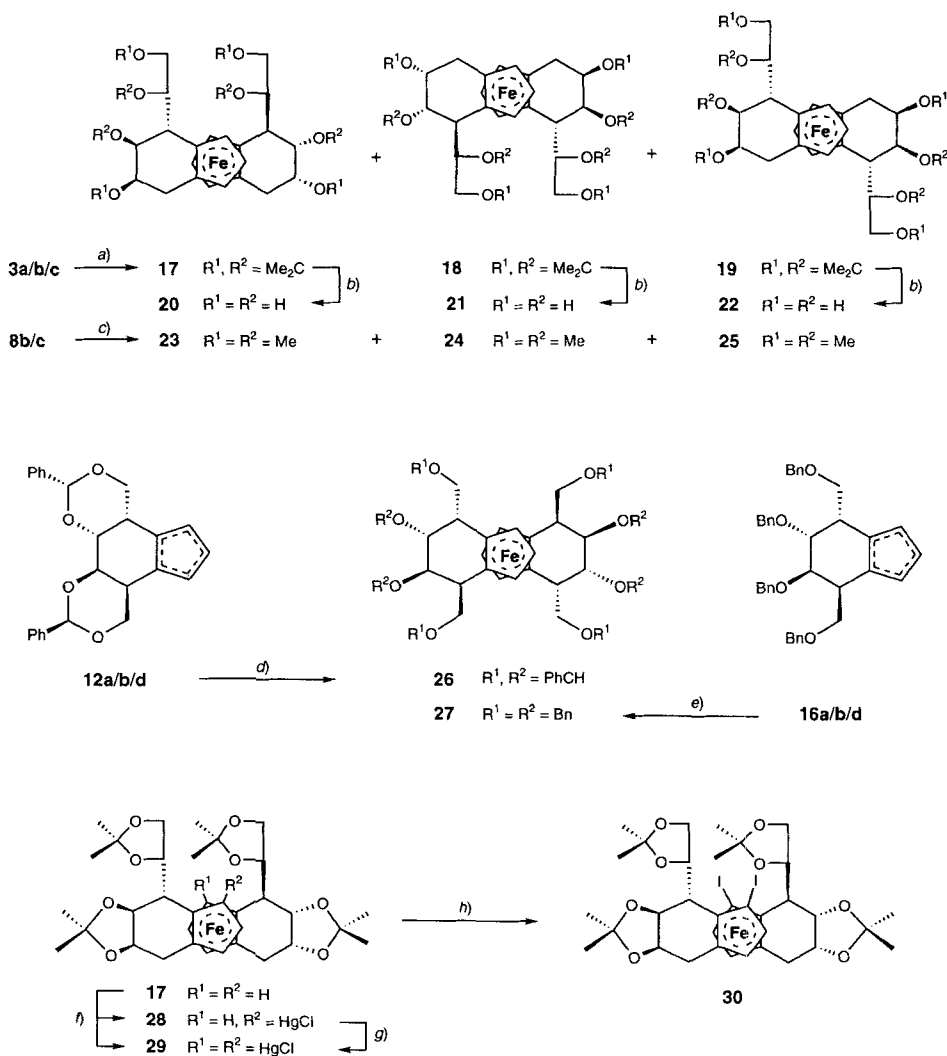
The 4,5,6,7-tetrahydro-1*H*- and -2*H*-indene structure of **3a/b/c** and **8b/c** is revealed by signals for two olefinic H and a CH₂ group exhibiting the characteristic large J_{gem} of 22–24 Hz (Table 1; cf. [24]). In **a**, the CH₂ group is inserted between the olefinic CH groups, as shown by the 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 ¹H-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 CH₂ group of **b** to the asymmetric centre C(i) should lead to a large $\Delta\delta$ for the CH₂ group and a small $\Delta\delta$ for the olefinic H-atoms; for **c**, one expects a small $\Delta\delta$ for the CH₂ group and a large $\Delta\delta$ for the olefinic H-atoms. Large $\Delta\delta$ values are indeed observed for the CH₂ 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 CH₂ 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 ¹³C-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 C₂-symmetric spirocyclopentadienes **11** and **15** may lead to four fused cyclopentadienes; i.e., the C₂-symmetric 2*H*-indene **a**, and the C₁-symmetric 1*H*-indene **b** (identical to **c**), and two C₁-symmetric 4*H*-indenes (only the *trans*-isomer **d** is shown in Scheme 1). Thus, the structures of **12a** and **16a** (C₂-symmetric), **12b** and **16b** (C₁-symmetric, 2 olefinic H and 1 allylic CH₂), and **12d** and **16d** are easily assigned (**12d** and **16d**: C₁-symmetric, 3 olefinic H and 1 allylic CH, strong upfield shift of H–C(i); the large $J(\text{a,i})$ of 12.1 (**12d**) and 11.0 Hz (**16d**) indicates the *trans*-arrangement of H–C(a) and H–C(i)). The ¹H-NMR spectra of **12a/b/d** and **16a/b/d** (Table 1) and the ¹³C-NMR spectra of **12b** and **16b** (Table 2) agree well with this assignment.

The cyclohexane ring adopts a ^{4*t*}*B* conformation in **3a/b/c** (as evidenced by medium $J(\text{f}_\text{A,g})$, $J(\text{f}_\text{B,g})$, and $J(\text{h,i})$; corresponding to dihedral angles of *ca.* 60°; Table 1), a ^{8*H*}*H*_h conformation in **8c** (as evidenced by the large $J(\text{f}_\text{B,g})$ of 9 Hz and the small $J(\text{h,i})$ of 2.4 Hz; overlap of signals prevents the analysis of **8b**), and again a ^{8*H*}*H*_h conformation in **12d** and **16d** (evidenced by the rather small $J(\text{f,g})$ and $J(\text{h,i})$ 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, $-60^\circ \rightarrow \text{r.t.}$; FeCl_2 , $-40^\circ \rightarrow \text{r.t.}$; 73%. b) 37% HCl, MeOH; 71% of **20**; 91% of **21**; 66% of **22**. c) BuLi, THF, $-80^\circ \rightarrow \text{r.t.}$; FeCl_2 , $-80^\circ \rightarrow \text{r.t.}$; 70%. d) BuLi, THF, $-40^\circ \rightarrow \text{r.t.}$; FeCl_2 , $-60^\circ \rightarrow \text{r.t.}$; 31%. e) BuLi, THF, $-78^\circ \rightarrow -35^\circ$; FeCl_2 , $-78^\circ \rightarrow \text{r.t.}$; 27%. f) $\text{Hg}(\text{OAc})_2$, 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 ^{1,3}*B* conformation as already observed for the related cyclopentadienes.

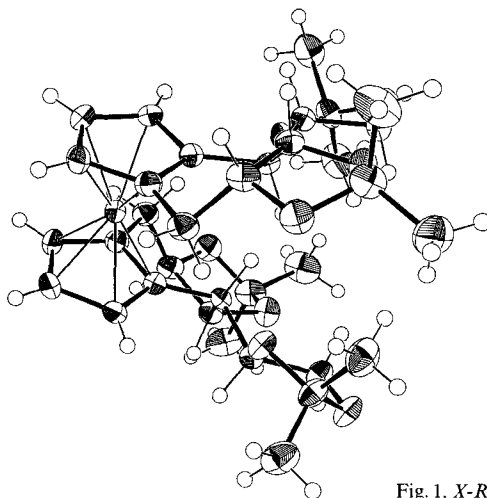


Fig. 1. X-Ray structure of **18**

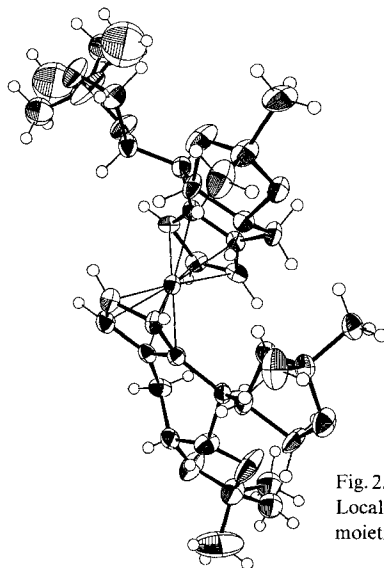


Fig. 2. X-Ray structure of **19**.
Local disorder of two isopropylidene
moieties.

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 H₂O-soluble: 20 mg of **20** dissolve freely in 0.05 ml of H₂O, 16 mg of **21** in 0.2 ml of H₂O, and 30 mg of **22** in 0.1 ml of H₂O. Lack of material prevented the preparation of saturated solutions.

Deprotonation of the *O*-methyl-protected cyclopentadienes **8b/c** with BuLi followed by treatment with FeCl₂ 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 C₂-symmetry of the (*S,S'*)_m-ferrocenes **17**, **20**, and **23**, and the (*R,R'*)_m-isomers **18**, **21**, and **24**, and the C₁-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 ^{6j}*B* conformation in the isopropylidene derivatives **17–19** and a ⁸*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**; C₂ 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 ¹H-NMR (CDCl₃) 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
<i>J</i> (f _A ,f _B)	15.4	14.4	14.3	14.4	15.0	14.5	14.7	14.7
<i>J</i> (f _A ,g)	8.0	7.8	6.9	8.4	4.6	10.0	3.9	8.9
<i>J</i> (f _B ,g)	6.5	8.4	8.6	7.2	8.2	5.5	8.0	5.3
<i>J</i> (g,h)	7.2	7.7	8.0	8.0	1.8	2.4	1.8	2.5
<i>J</i> (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 ¹³C-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 FeCl₂ led to the expected single, C₂-symmetric ferrocene **26** (31%). Similar treatment of the cyclopentadienes

16a/b/d with BuLi and FeCl₂ afforded the C₂-symmetric ferrocene **27** (27%). The C₂-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 C₂-symmetric ferrocene **17** followed by treatment with LiCl gave the C₂-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 C₂-symmetric 1,1'-diiodoferrocene **30** was obtained in 93% yield by the reaction of the bis(chloromercurio)ferrocene **29** with *N*-iodosuccinimide (NIS).

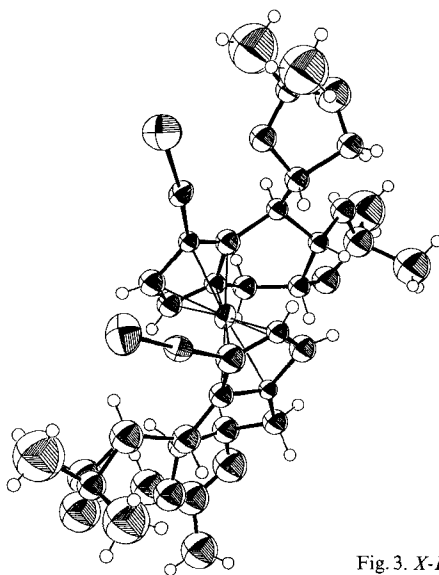


Fig. 3. X-Ray structure of **29**

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 ¹³C-NMR spectrum of C₂-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%), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ (5%), and $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ (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 , $250 \times 4.6 \text{ mm}$ column), Nucleosil 5 CN (5 μm , $250 \times 4.0 \text{ mm}$ column), UV detection (254 nm), 2 ml/min; prep. Spherisorb silica gel (5 μm , $250 \times 20 \text{ mm}$ column), Nucleosil 5 CN (5 μm , $250 \times 21 \text{ mm}$ column), 16 ml/min. M.p.: uncorrected. Optical rotations: 1-dm cell at 25° at 589 nm. IR Spectra: in CHCl_3 or KBr. ^1H - and ^{13}C -NMR Spectra: at 200, 300 (^1H), and at 75 MHz (^{13}C); chemical shifts δ in ppm rel. to SiMe_4 , coupling constants J in Hz; ^1H -assignments were corroborated by selective homonuclear decoupling experiments. Mass spectra: EI at 70 V or FAB.

(3*a*S,4*S*,6*a*R,4'*S*) -4-(2',2'-Dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,4,6,6*a*-tetrahydro-2,2-dimethylspiro[5*H*-cyclopenta-1,3-dioxole-5,1'-cyclopenta-2',4'-diene] (**2**). CpNa in THF (2*M*, 1.46 ml, 2.92 mmol) was added dropwise to a suspension of NaH (60% in mineral oil; washed with $3 \times 2 \text{ ml}$ 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. $34.5\text{--}36.5^\circ$. $[\alpha]_D^{25} = +11.7$ ($c = 1.115$, CHCl_3). IR (CHCl_3): 2990s, 2936s, 1456*m*, 1382s, 1373s, 1159s, 1129w, 1057s, 966w, 853*m*. ^1H -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*, $J = 6.8, 5.0$, $\text{H}-\text{C}(6a)$); 4.63 (*dd*, $J = 6.8, 5.0$, $\text{H}-\text{C}(3a)$); 3.93–3.85 (*m*, $\text{H}-\text{C}(4'')$, $\text{H}_A-\text{C}(5'')$); 3.64 (*dd*, $J = 10.5, 9.6$, $\text{H}_B-\text{C}(5'')$); 2.58 (*t*, $J = 5.3$, $\text{H}-\text{C}(4)$); 2.04 (*dd*, $J = 13.3, 5.0$, $\text{H}_A-\text{C}(6)$); 1.93 (*dd*, $J = 13.3, 6.5$, $\text{H}_B-\text{C}(6)$); 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, $[M - \text{Me}]^+$), 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 $\text{C}_{17}\text{H}_{24}\text{O}_4$ (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**.

(3*a*S,4*S*,8*a*R,4'*S*) -4-(2',2'-Dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,6,8,8*a*-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): 3008s, 2985s, 2933w, 2890*m*, 1456*m*, 1380s, 1370s, 1160s, 1060s, 990w, 970w, 930w, 905*m*, 890*m*, 855*m*. ^1H -NMR (300 MHz, CDCl_3): 6.28 (br. *s*, $w_{1/2} = 5$, $\text{H}-\text{C}(7)$); 6.07 (br. *s*, $w_{1/2} = 5$, $\text{H}-\text{C}(5)$); 4.37 (*td*, $J = 7.5, 5.9$, $\text{H}-\text{C}(8a)$); 4.35 (*td*, $J \approx 8.0, 6.3$, $\text{H}-\text{C}(4')$); 4.14 (*dd*, $J = 8.3, 6.1$, $\text{H}_A-\text{C}(5')$); 4.12 (*t*, $J = 7.1$, $\text{H}-\text{C}(3a)$); 3.85 (*t*, $J = 8.3$, $\text{H}_B-\text{C}(5')$); 3.04 (br. *d*, $J \approx 24$, $\text{H}_A-\text{C}(6)$); 3.02–2.94 (*m*, $\text{H}_A-\text{C}(8)$); 2.95 (br. *d*, $J \approx 24$, $\text{H}_B-\text{C}(6)$); 2.79 (*tt*, $J \approx 7.0, 2.1$, $\text{H}-\text{C}(4)$); 2.54 (*ddt*, $J = 14.4, 7.5, 2.2$, $\text{H}_B-\text{C}(8)$); 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*).

(3*a*S,4*S*,8*a*R,4'*S*) -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-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): 3008s, 2990s, 2936*m*, 1602w, 1456*m*, 1382s, 1372s, 1157s, 1055s, 967w, 950w, 895w, 854*m*. ^1H -NMR (300 MHz, CDCl_3): 6.35 (br. *s*, $\text{H}-\text{C}(6)$, $\text{H}-\text{C}(7)$); 4.46 (*td*, $J = 6.2, 4.0$, $\text{H}-\text{C}(8a)$); 4.23 (*q*, $J \approx 7.0$, $\text{H}-\text{C}(4')$); 4.16 (*dd*, $J = 5.9, 4.1$, $\text{H}-\text{C}(3a)$); 4.16 (*dd*, $J = 8.3, 6.4$, $\text{H}_A-\text{C}(5')$); 3.75 (*dd*, $J = 8.4, 7.2$, $\text{H}_B-\text{C}(5')$); 3.11 (br. *d*, $J = 24$, $\text{H}_A-\text{C}(5)$); 3.00 (br. *d*, $J = 24$, $\text{H}_B-\text{C}(5)$); 2.87–2.80 (*m*, $\text{H}-\text{C}(4)$); 2.78 (br. *dd*, $J = 17.4, 6.6$, $\text{H}_A-\text{C}(8)$); 2.55 (br. *d*, $J = 17.4$, $\text{H}_B-\text{C}(8)$); 1.41 (*s*, Me); 1.40 (*s*, Me); 1.37 (*s*, 2 Me).

(3*a*S,4*S*,8*a*R,4'*S*) -4-(2',2'-Dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,7,8,8*a*-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): 3008s, 2980s, 2936*m*, 2901*m*, 1602w, 1456w, 1382s, 1372s, 1163s, 1053s, 968w, 948w, 869*m*, 849w. ^1H -NMR (300 MHz, CDCl_3): 6.53 (br. *d*, $J = 5.4$, $\text{H}-\text{C}(5)$); 6.29 (br. *d*, $J = 5.4$, $\text{H}-\text{C}(6)$); 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, $[M - \text{Me}]^+$), 159 (4), 131 (3), 115 (3), 101 (100), 91 (7), 43 (8). Anal. calc. for C₁₇H₂₄O₄ (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 NaBH₄ (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 (CH₂Cl₂/MeOH 9:1) afforded **5** (906 mg, 84%). White microcrystalline powder. R_f (CH₂Cl₂/MeOH 9:1) 0.56. M_p 30–31.5°. $[\alpha]_D^{25} = -11.4$ ($c = 1.06$, CHCl₃). IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 3.88 (*br. dt*, $J \approx 11.8, 4.2$, addn. of D₂O → *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 D₂O → 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 D₂O, HO-C(3)); 2.39 (*br. dd*, $J = 7.4, 4.4$, exchange with D₂O, HO-C(6)). ¹³C-NMR (75 MHz, CDCl₃): 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 C₁₀H₂₂O₆ (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 Et₃N (0.80 ml, 5.77 mmol) in dry CH₂Cl₂ (5 ml) was treated with MsCl (0.44 ml, 5.67 mmol), stirred for 1 h at 0°, and treated with sat. aq. NaHCO₃ soln. (5 ml). Normal workup afforded **6** (569 mg, 99%) as an oil. R_f (CHCl₃/MeOH 95:5) 0.62. $[\alpha]_D^{25} = +21.1$ ($c = 1.05$, CHCl₃). IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 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). ¹³C-NMR (75 MHz, CDCl₃): 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 C₁₇H₂₆O₁₀S₂ (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 2*M* 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 H₂O (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. $[\alpha]_D^{25} = -4.6$ ($c = 1.06$, CHCl₃). IR (CHCl₃): 3007*s*, 2930*m*, 2830*m*, 1516*w*, 1450*m*, 1370*m*, 1124*s*, 1083*s*, 1009*w*, 977*w*. ¹H-NMR (300 MHz, CDCl₃): 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)). ¹³C-NMR (75 MHz, CDCl₃): 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 C₁₅H₂₄O₄ (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). CDCl₃ 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. $[\alpha]_D^{25} = -5.8$ ($c = 0.71$, CHCl₃). IR (CHCl₃): 3007*s*, 2930*m*, 2896*m*, 2828*m*, 1708*w*, 1603*w*, 1456*m*, 1377*m*, 1096*s*, 1009*w*, 968*w*, 895*w*. ¹H-NMR (200 MHz, CDCl₃): 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)). ¹³C-NMR (50 MHz, CDCl₃): 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*).

(4*S*,5*S*,6*R*,1'*S*)-4-(1',2'-Dimethoxyethyl)-4,5,6,7-tetrahydro-5,6-dimethoxy-1*H*-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*. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 6.37 (br. *d*, $J = 5.4$, $\text{H-C}(3)$); 6.23 (br. *d*, $J = 5.4$, $\text{H-C}(2)$); 3.69 (*t*, $J \approx 2.4$, $\text{H-C}(5)$); 3.61 (*dd*, $J = 8.6$, 5.9, 2.2, $\text{H-C}(6)$); 3.51–3.45 (*m*, $\text{H-C}(1')$, 2 $\text{H-C}(2')$); 3.45 (*s*, Me); 3.43 (*s*, Me); 3.41 (*s*, Me); 3.38 (*s*, Me); 3.04–2.95 (br. *s*, $w_{1/2} = 10$, $\text{H-C}(4)$); 2.87 (br. *s*, 2 $\text{H-C}(1)$); 2.64 (*dd*, $J = 17.0$, 5.8, $\text{H}_A\text{-C}(7)$); 2.52 (*dd*, $J = 17.0$, 9.0, $\text{H}_B\text{-C}(7)$). $^{13}\text{C-NMR}$ (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^+), 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 $\text{C}_{15}\text{H}_{24}\text{O}_4$ (268.35): C 67.14, H 9.01; found: C 67.39, H 9.25.

(2*R*,4*aS*,5*aS*,8*R*,9*aR*,9*bR*)-4*a*,5*a*,6,9*a*,9*b*-Hexahydro-2,8-diphenylspiro[5*H*-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 2*M* 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/Et₂O 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*. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.55–7.51 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.78 (*d*, $J = 6.5$, $\text{H-C}(1')$); 5.53 (*s*, $\text{H-C}(2)$); 4.55 (*d*, $J = 3.1$, $\text{H-C}(9b)$); 4.04 (*dd*, $J = 12.1$, 3.5, $\text{H}_A\text{-C}(4)$); 3.64 (*d*, $J = 12.1$, $\text{H}_B\text{-C}(4)$); 2.91 (*t*, $J = 3.4$, $\text{H-C}(4a)$). $^{13}\text{C-NMR}$ (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^+), 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 $\text{C}_{25}\text{H}_{24}\text{O}_4$ (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/Et₂O 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.

(2*R*,4*aS*,7*bS*,10*R*,11*aR*,11*bR*)-4*a*,6,7*b*,8,11*a*,11*b*-Hexahydro-2,10-diphenyl-4*H*-indenof[5,4-*d*:6,7-*d'*]bis-[1,3]dioxin (**12a/b** 7:93): R_f (hexane/Et₂O 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*. $^1\text{H-NMR}$ (300 MHz, CDCl_3): signals of **12b**: 7.43–7.33 (*m*, 10 arom. H); 6.64 (*d*, $J = 5.4$, $\text{H-C}(7)$); 6.46 (*dd*, $J = 5.4$, 1.1, $\text{H-C}(6)$); 5.63, 5.625 (2*s*, $\text{H-C}(2)$, $\text{H-C}(10)$); 4.66, 4.55 (2*dd*, each $J = 11.8$, 1.1, $\text{H}_A\text{-C}(4)$, $\text{H}_B\text{-C}(8)$); 4.51–4.44 (*m*, $\text{H-C}(11a)$, $\text{H-C}(11b)$); 4.233 (*dd*, $J = 11.8$, 3.2), 4.228 (*dd*, $J = 11.7$, 2.8, $\text{H}_B\text{-C}(4)$, $\text{H}_B\text{-C}(8)$); 3.25 (br. *d*quint., $J \approx 23$, 1.5, $\text{H}_A\text{-C}(5)$); 3.03 (br. *d*, $J \approx 23$, $\text{H}_B\text{-C}(5)$); 2.78 (br. *s*, $w_{1/2} = 8$), 2.69 (br. *s*, $w_{1/2} = 10$, $\text{H-C}(4a)$, $\text{H-C}(7b)$); signals of **12a**: 6.37 (br. *q*, $J = 1.75$, $\text{H-C}(5)$); 5.65 (*s*, $\text{H-C}(2)$); 4.29 (br. *d*, $J = 1.8$, $\text{H-C}(11b)$); 3.12–3.08 (br. *s*, $\text{H-C}(6)$); 2.88–2.83 (br. *s*, $\text{H-C}(4a)$). $^{13}\text{C-NMR}$ (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*).

(2*R*,4*aS*,4*bS*,7*bS*,10*R*,11*aR*,11*bR*)-4*a*,4*b*,7*b*,8,11*a*,11*b*-Hexahydro-2,10-diphenyl-4*H*-indenof[5,4-*d*:6,7-*d'*]bis[1,3]dioxin (**12d**): R_f (hexane/Et₂O 9:1) 0.23. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.56–7.29 (*m*, 10 arom. H); 6.62 (*dt*, $J = 5.4$, 1.4, $\text{H-C}(6)$); 6.57 (*dd*, $J = 5.4$, 0.9, $\text{H-C}(7)$); 6.48 (*t*, $J = 1.4$, $\text{H-C}(5)$); 5.69, 5.57 (2*s*, $\text{H-C}(2)$, $\text{H-C}(10)$); 4.71, 4.39 (2 br. *d*, each $J = 12.4$, $\text{H}_A\text{-C}(4)$, $\text{H}_B\text{-C}(8)$); 4.42 (*t*, $J \approx 2.8$), 4.21 (*t*, $J \approx 2.8$, $\text{H-C}(11a)$, $\text{H-C}(11b)$); 4.19 (*dd*, $J = 12.0$, 2.8), 4.18 (*dd*, $J = 12.2$, 2.5, $\text{H}_B\text{-C}(4)$, $\text{H}_B\text{-C}(8)$); 3.71 (br. *d*, $J = 12.1$, $\text{H-C}(4b)$); 2.80 (br. *s*, $\text{H-C}(7b)$); 1.42 (br. *d*, $J = 12.1$, $\text{H-C}(4a)$).

Data of 12a/b/d: EI-MS: 388 (5, M^+), 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 $\text{C}_{25}\text{H}_{24}\text{O}_4$ (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_2 (60 ml) was treated with Et₃N (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. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.34–7.25 (*m*, 10 arom. H); 4.95 (*dt*, $J = 6.8$, 3.4, $\text{H-C}(2)$); 4.70 (*d*, $J = 11.8$, PhCH); 4.63 (*d*, $J = 11.8$, PhCH); 4.54 (*d*, $J = 11.8$, PhCH); 4.47 (*d*, $J = 11.8$, PhCH); 4.05–3.99 (*m*, $\text{H-C}(3)$); 3.90 (*dd*, $J = 11.2$, 3.2, $\text{H}_A\text{-C}(1)$); 3.79 (*dd*, $J = 11.2$, 7.0, $\text{H}_B\text{-C}(1)$); 2.94 (*s*, 2 *Ms*).

(6*S*,7*R*,8*R*,9*S*)-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 2*M* 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. $[\alpha]_D^{25} = +82.8$ ($c = 1.09$, CHCl₃). IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 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*, $J = 12.0$, PhCH); 4.55 (*d*, $J = 12.0$, PhCH); 4.54 (*d*, $J = 11.9$, PhCH); 4.38 (*d*, $J = 11.9$, PhCH); 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)). ¹³C-NMR (75 MHz, CDCl₃): 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 C₃₉H₄₀O₄ (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**.

(4*S*,5*R*,6*R*,7*S*)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-4,5,6,7-tetrahydro-2*H*-indene (**16a**): R_f (hexane/AcOEt 9:1) 0.30. IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 7.40–7.20 (*m*, 10 arom. H); 6.14 (*br. d*, $J = 1.7$, H–C(1)); 4.58 (*d*, $J = 12.0$, PhCH); 4.52 (*d*, $J = 12.0$, PhCH); 4.50 (*s*, PhCH₂); 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)).

(4*S*,5*R*,6*R*,7*S*)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-4,5,6,7-tetrahydro-1*H*-indene (**16b**): R_f (hexane/AcOEt 9:1) 0.27. IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 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 PhCH₂); 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)). ¹³C-NMR (75 MHz, CDCl₃): 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*).

(3*aS*,4*S*,5*R*,6*R*,7*S*)-5,6-Bis(benzyloxy)-4,7-bis[(benzyloxy)methyl]-3*a*,5,6,7-tetrahydro-4*H*-indene (**16d**): R_f (hexane/AcOEt 9:1) 0.35. IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 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*, PhCH₂); 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(3*a*)); 1.91–1.78 (*m*, H–C(4)).

Data of **16a/b/d**: $[\alpha]_D^{25} = -15.6$ ($c = 1.05$, CHCl₃). 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 C₃₉H₄₀O₄ (572.75): C 81.79, H 7.04; found: C 81.90, H 6.90.

Reaction of 3a/b/c with BuLi and FeCl₂. 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 1.5*M* 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 FeCl₂ (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{[4*a*,5,6,7,7*a*-η]-(3*aS*,4*S*,8*aR*,4"*S*)-4-(2",2"-dimethyl-1",3"-dioxolan-4"-yl)-3*a*,5,8,8*a*-tetrahydro-2,2-dimethyl-4*H*-indenol[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°. $[\alpha]_D^{25} = -180.3$ ($c = 0.80$, CHCl₃). IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 4.65 (*q*, $J = 7.2$, H–C(8*a*)); 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(3*a*)); 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). ¹³C-NMR (75 MHz, CDCl₃): 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*⁺), 231 (6), 187 (9), 171 (5), 129 (6), 115 (8), 101 (10), 58 (6), 43 (23). Anal. calc. for C₃₄H₄₆FeO₈ (638.58): C 63.95, H 7.26; found: C 63.87, H 7.35.

(*R,R'*)_m-Bis[(4*a*,5,6,7,7*a*-η)-(3*a*S,4*S*,8*a*R,4"*S*)-4-(2'',2''-dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,5,8,8*a*-tetrahydro-2,2-dimethyl-4*H*-indenol[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°. [α]_D²⁵ = +230.1 (*c* = 0.99, CHCl₃). IR (CHCl₃): 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*. ¹H-NMR (300 MHz, CDCl₃): 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(8*a*)); 3.97 (*t*, *J* = 8.2, H_B–C(5'')); 3.86 (*t*, *J* = 7.7, H–C(3*a*)); 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). ¹³C-NMR (75 MHz, CDCl₃): 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*⁺), 231 (6), 175 (4), 159 (6), 117 (7), 101 (38), 58 (8), 43 (35). Anal. calc. for C₃₄H₄₆FeO₈ (638.58): C 63.95, H 7.26; found: C 64.06, H 7.11.

(*R,S'*)_m-Bis[(4*a*,5,6,7,7*a*-η)-(3*a*S,4*S*,8*a*R,4"*S*)-4-(2'',2''-dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,5,8,8*a*-tetrahydro-2,2-dimethyl-4*H*-indenol[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°. [α]_D²⁵ = –44.6 (*c* = 0.92, CHCl₃). IR (CHCl₃): 2989*m*, 2937*w*, 2886*w*, 1456*w*, 1382*s*, 1372*m*, 1161*m*, 1055*s*, 967*w*, 918*w*, 889*w*, 844*w*. ¹H-NMR (300 MHz, CDCl₃): 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(8*a*)); 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(3*a*)); 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). ¹³C-NMR (75 MHz, CDCl₃): 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*⁺), 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 C₃₄H₄₆FeO₈ (638.58): C 63.95, H 7.26; found: C 63.98, H 7.18.

(*S,S'*)_m-Bis[(1,2,3,3*a*,7*a*-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 (CH₂Cl₂/MeOH 6:4) gave **20** (29 mg, 71%) as a yellow oil (20 mg of **20** dissolved freely in 0.05 ml of H₂O). *R*_f (CH₂Cl₂/MeOH 6:4) 0.24. [α]_D²⁵ = –24.3 (*c* = 0.99, MeOH). ¹H-NMR (300 MHz, CD₃OD): 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). ¹³C-NMR (75 MHz, CD₃OD): 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 (NH₃): 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[(1,2,3,3*a*,7*a*-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 H₂O). *R*_f (MeOH/AcOEt 1:1) 0.37. M.p. 111–113°. [α]_D²⁵ = +57.6 (*c* = 0.40, MeOH). ¹H-NMR (300 MHz, CD₃OD/D₂O): 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)). ¹³C-NMR (75 MHz, CD₃OD/D₂O): 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 (NH₃): 479 (17, [*M* + 1]⁺), 478 (17, *M*⁺), 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[(1,2,3,3*a*,7*a*-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 (CH₂Cl₂/MeOH 1:1) gave **22** (44.3 mg, 66%) as a yellow oil (30 mg of **22** dissolved freely in 0.1 ml of H₂O). *R*_f (CH₂Cl₂/MeOH 6:4) 0.38. ¹H-NMR (200 MHz, CD₃OD): 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). $^{13}\text{C-NMR}$ (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, $[\text{M} + 1]^+$), 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 mmol) in dry THF (10 ml) was degassed, treated with 1.5*M* 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 $\rightarrow$ 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 ($^1\text{H-NMR}$) samples of **23–25**.

($\text{S,S}'$)_{*m*}-*Bis*[(1,2,3,3*a*,7*a*-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*. $^1\text{H-NMR}$ (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)).

($\text{R,R}'$)_{*m*}-*Bis*[(1,2,3,3*a*,7*a*-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*. $^1\text{H-NMR}$ (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)). $^{13}\text{C-NMR}$ (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*).

($\text{R,S}'$)_{*m*}-*Bis*[(1,2,3,3*a*,7*a*-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*. $^1\text{H-NMR}$ (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* $\approx$ 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)). $^{13}\text{C-NMR}$ (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^+), 323 (7), 229 (6), 203 (9), 172 (14), 141 (17), 115 (15), 89 (10), 59 (5). Anal. calc. for $\text{C}_{30}\text{H}_{46}\text{FeO}_8$ (590.54): C 61.02, H 7.85; found: C 60.91, H 7.98.

Bis[(4*b*,5,6,7,7*a*-η)-(2*R*,4*aS*,7*bS*,10*R*,11*aR*,11*bR*)-4*a*,4*b*,7*b*,8,11*a*,11*b*-hexahydro-2,10-diphenyl-4*H*-inden-4,5-d:6,7-d']bis[1,3-dioxin-4*b*-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 1.5*M* 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*. $^1\text{H-NMR}$ (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(11*a*), H-C(11*b*), 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(7*b*)); 2.55 (*t*, *J* = 3.8, H-C(4*a*)). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 138.38 (*s*); 138.15 (*s*); 128.77 (*d*); 128.49 (*d*); 128.13 (*2d*); 128.06 (*2d*); 126.11 (*2d*); 125.84 (*2d*); 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^+), 586 (5), 443 (28), 277 (5), 199 (6), 171 (22), 129 (9), 105 (88), 77 (59).

Bis[(1,2,3,3*a*,7*a*-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 1.6*M* 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): 3088w, 3066w, 3008s, 2918m, 2866s, 1496m, 1454s, 1362s, 1329w, 1099s, 1071s, 1047m, 1028m, 928w, 910w. $^1\text{H-NMR}$ (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, $J = 11.8$, PhCH); 4.41 (s, PhCH_2); 4.39 (d, $J = 11.8$, PhCH); 4.08 (t, $J = 9.0$, $\text{CH}_A\text{--C}(4)$); 4.02–3.98 (m, $\text{H--C}(5)$); 3.97 (br. s, 1 arom. H); 3.92 (t, $J = 4.1$, $\text{H--C}(6)$); 3.84 (dd, $J = 8.8$, 5.2, $\text{CH}_B\text{--C}(4)$); 3.76 (br. s, 2 arom. H); 3.57 (br. s, $\text{H--C}(4)$); 3.50–3.47 (m, $\text{CH}_2\text{--C}(7)$); 3.00–2.98 (m, $\text{H--C}(7)$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 138.74 (2s); 138.64 (s); 138.49 (s); 128.33 (d); 128.26 (5d); 128.12 (3d); 128.00 (3d); 127.62 (3d); 127.50 (d); 127.44 (3d); 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 $\text{Hg}(\text{OAc})_2$ (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 $\rightarrow$ 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') $_m$ -{(4*a*,5,6,7,7*a*- η)-(3*aS*,4*S*,8*aR*,4"*S*)-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)}{(4'*a*,5',6',7',7'*a*- η)-(3'*aS*,4'*S*,8'*aR*,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): 3008w, 2990m, 2936m, 1709w, 1602w, 1456m, 1382s, 1374s, 1158s, 1054s, 966w, 911w, 886m, 839m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 4.62 (dd, $J = 7.5$, 4.4), 4.57 (dd, $J = 7.3$, 4.4, $\text{H--C}(8a)$, $\text{H--C}(8'a)$); 4.61 (d, $J = 2.6$, 1 arom. H); 4.40–4.32 (m, $\text{H--C}(4'')$, $\text{H--C}(4''')$); 4.28 (dd, $J = 8.9$, 5.7), 4.25 (dd, $J = 8.7$, 5.6, $\text{H}_A\text{--C}(5'')$, $\text{H}_A\text{--C}(5''')$); 4.20 (t, $J = 7.2$), 4.13 (t, $J = 7.2$, $\text{H--C}(3a)$, $\text{H--C}(3'a)$); 4.16 (dd, $J = 8.7$, 7.7), 4.03 (dd, $J = 8.7$, 7.4, $\text{H}_B\text{--C}(5'')$, $\text{H}_B\text{--C}(5''')$); 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, $\text{H}_A\text{--C}(8)$, $\text{H}_A\text{--C}(8')$); 2.49, 2.45 (dd, each $J = 9.4$, 7.4, $\text{H--C}(4)$, $\text{H--C}(4')$); 2.31 (dd, $J = 15.0$, 7.7), 2.24 (dd, $J = 14.9$, 7.8, $\text{H}_B\text{--C}(8)$, $\text{H}_B\text{--C}(8')$); 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). $^{13}\text{C-NMR}$ (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 (2d); 69.69 (d); 68.60 (2t); 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{(4*a*,5,6,7,7*a*- η)-(3*aS*,4*S*,8*aR*,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) (**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): 3008w, 2991s, 2937m, 1733w, 1602m, 1456m, 1383s, 1374s, 1154s, 1054s, 1020w, 966w, 930w, 887s, 838s. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 4.55 (dt, $J \approx 9.0$, 6.9, $\text{H--C}(8a)$); 4.44–4.37 (m, $\text{H--C}(4'')$); 4.35 (d, $J = 2.2$, 1 arom. H); 4.29 (dd, $J = 9.1$, 6.0, $\text{H}_A\text{--C}(5'')$); 4.21 (t, $J \approx 7.8$, $\text{H}_B\text{--C}(5'')$); 4.19 (d, $J = 2.4$, 1 arom. H); 4.16 (t, $J = 7.1$, $\text{H--C}(3a)$); 2.73 (dd, $J = 14.6$, 6.7, $\text{H}_A\text{--C}(8)$); 2.52 (dd, $J = 9.6$, 6.9, $\text{H--C}(4)$); 2.17 (dd, $J = 14.6$, 9.2, $\text{H}_B\text{--C}(8)$); 1.63 (s, Me); 1.47 (s, Me); 1.46 (s, Me); 1.38 (s, Me). $^{13}\text{C-NMR}$ (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 (2d); 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), $\text{Hg}(\text{OAc})_2$ (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{(4*a*,5,6,7,7*a*- η)-(3*aS*,4*S*,8*aR*,4"*S*)-4-(2'',2''-dimethyl-1'',3''-dioxolan-4''-yl)-3*a*,5,8,8*a*-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 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): 3008w, 2989s, 2934m, 1723m, 1602w, 1455w, 1430w, 1382s, 1373s, 1159s, 1047s, 969w, 923w, 909w, 855m, 829w. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 4.50–4.44 (m, $\text{H--C}(8a)$); 4.43 (q, $J \approx 8.1$, $\text{H--C}(4'')$); 4.31 (dd, $J = 8.1$, 6.2, $\text{H}_A\text{--C}(5'')$); 4.24 (dd, $J = 4.4$, 1.7, $\text{H--C}(3a)$); 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 (*2q*); 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^+), 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) Å³; $D_x = 1.276$ Mg/m³; $Z = 3$. Intensities were measured in the ω -scan mode on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, MoK_{α} , $\lambda = 0.71073$ 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) Å³; $D_x = 1.290$ Mg/m³; $Z = 4$. 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) Å³; $D_x = 1.915$ Mg/m³; $Z = 4$. 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.

REFERENCES

- [1] R. L. Haltermann, *Chem. Rev.* **1992**, 92, 965.
- [2] T. Hayashi, in 'Ferrocenes', Eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995, p. 105.
- [3] Y. Butsugan, S. Araki, M. Watanabe, in 'Ferrocenes', Eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995, p. 143.
- [4] T. Hayashi, M. Tajika, K. Tamao, M. Kumada, *J. Am. Chem. Soc.* **1976**, 98, 3718; T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika, M. Kumada, *ibid.* **1982**, 104, 180; C. Cardellicchio, V. Fiandanesi, F. Naso, *Gazz. Chim. Ital.* **1991**, 121, 11; K. Tamao, T. Hayashi, H. Matsumoto, H. Yamamoto, M. Kumada, *Tetrahedron Lett.* **1979**, 2155; M. Zembayashi, K. Tamao, T. Hayashi, T. Mise, M. Kumada, *ibid.* **1977**, 1799; T. Hayashi, T. Hagihara, Y. Katsuro, M. Kumada, *Bull. Chem. Soc. Jpn.* **1983**, 56, 363; T. Hayashi, A. Yamamoto, M. Hojo, Y. Ito, *J. Chem. Soc., Chem. Commun.* **1989**, 495; T. Hayashi, M. Konishi, H. Ito, M. Kumada, *J. Am. Chem. Soc.* **1982**, 104, 4962; T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta, M. Kumada, *J. Org. Chem.* **1986**, 51, 3772; T. Hayashi, *Chem. Scr.* **1985**, 25, 61; T. Hayashi, K. Hayashizaki, T. Kiyoi, Y. Ito, *J. Am. Chem. Soc.* **1988**, 110, 8153; T. Hayashi, K. Hayashizaki, Y. Ito, *Tetrahedron Lett.* **1989**, 30, 215.
- [5] T. Hayashi, K. Kanehira, T. Hagihara, M. Kumada, *J. Org. Chem.* **1988**, 53, 113; Y. Ito, M. Sawamura, M. Matsuoka, M. Matsumoto, T. Hayashi, *Tetrahedron Lett.* **1987**, 28, 4849; M. Sawamura, H. Nagata, H. Sakamoto, Y. Ito, *J. Am. Chem. Soc.* **1992**, 114, 2586; T. Hayashi, A. Yamamoto, T. Hagihara, Y. Ito, *Tetrahedron Lett.* **1986**, 27, 191; T. Hayashi, *Pure Appl. Chem.* **1988**, 60, 7; T. Hayashi, A. Yamamoto, Y. Ito, *Chem. Lett.* **1987**, 117; T. Hayashi, A. Yamamoto, Y. Ito, *J. Chem. Soc., Chem. Commun.* **1986**, 1090; T. Hayashi, K. Kishi, A. Yamamoto, Y. Ito, *Tetrahedron Lett.* **1990**, 31, 1743; T. Hayashi, A. Yamamoto, Y. Ito, *ibid.* **1988**, 29, 99; A. Yamamoto, Y. Ito, T. Hayashi, *ibid.* **1989**, 30, 375; Y. Matsumoto, A. Ohno, T. Hayashi, *Organometallics* **1993**, 12, 4051; T. Takemoto, Y. Nishikimi, M. Sodeoka, M. Shibasaki, *Tetrahedron Lett.* **1992**, 33, 3531.
- [6] Y. Ito, M. Sawamura, T. Hayashi, *J. Am. Chem. Soc.* **1986**, 108, 6405; A. Togni, S. D. Pastor, G. Rihs, *J. Organomet. Chem.* **1990**, 381, C21; Y. Ito, M. Sawamura, T. Hayashi, *Tetrahedron Lett.* **1987**, 28, 6215; T. Hayashi, M. Sawamura, Y. Ito, *Tetrahedron* **1992**, 48, 1999; A. Togni, R. E. Blumer, P. S. Pregosin, *Helv. Chim. Acta* **1991**, 74, 1533; S. D. Pastor, A. Togni, *J. Am. Chem. Soc.* **1989**, 111, 2333; A. Togni, S. D. Pastor, *J. Org. Chem.* **1990**, 55, 1649; A. Togni, R. Häusel, *Synlett* **1990**, 633; A. Togni, G. Rihs, R. E. Blumer, *Organometallics* **1992**, 11, 613; S. D. Pastor, A. Togni, *Tetrahedron Lett.* **1990**, 31, 839; S. D. Pastor, A. Togni, *Helv. Chim. Acta* **1991**, 74, 905; S. D. Pastor, R. Kesselring, A. Togni, *J. Organomet. Chem.* **1992**, 429, 415; Y. Ito, M. Sawamura, M. Kobayashi, T. Hayashi, *Tetrahedron Lett.* **1988**, 29, 6321; Y. Ito, M. Sawamura,

- H. Hamashima, T. Emura, T. Hayashi, *ibid.* **1989**, 30, 4681; Y. Ito, M. Sawamura, E. Shirakawa, K. Hayashizaki, T. Hayashi, *ibid.* **1988**, 29, 235; Y. Ito, M. Sawamura, E. Shirakawa, K. Hayashizaki, T. Hayashi, *Tetrahedron* **1988**, 44, 5253; A. Togni, S.D. Pastor, *Tetrahedron Lett.* **1989**, 30, 1071; M. Sawamura, Y. Ito, T. Hayashi, *ibid.* **1989**, 30, 2247.
- [7] K. Yamamoto, J. Wakatsuki, R. Sugimoto, *Bull. Chem. Soc. Jpn.* **1980**, 53, 1132; W.R. Cullen, W.B. Einstein, C.-H. Huang, A.C. Willis, E.-S. Yeh, *J. Am. Chem. Soc.* **1980**, 102, 988; W.R. Cullen, J.D. Woollins, *Can. J. Chem.* **1982**, 60, 1793; T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, M. Kumada, *Tetrahedron Lett.* **1976**, 1133; H. Brunner, B. Schönhammer, C. Steinberger, *Chem. Ber.* **1983**, 116, 3529.
- [8] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, 116, 4062.
- [9] T. Hayashi, N. Kawamura, Y. Ito, *J. Am. Chem. Soc.* **1987**, 109, 7876; T. Hayashi, N. Kawamura, T. Ito, *Tetrahedron Lett.* **1988**, 29, 5969; T. Hayashi, T. Mise, M. Kumada, *ibid.* **1976**, 4351; T. Hayashi, A. Katsumura, M. Konishi, M. Kumada, *ibid.* **1979**, 425.
- [10] T. Hayashi, K. Tamao, Y. Katsuro, I. Nakae, M. Kumada, *Tetrahedron Lett.* **1980**, 21, 1871; T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao, M. Kumada, *ibid.* **1983**, 24, 5661; T. Hayashi, K. Kabeta, *ibid.* **1985**, 26, 3023; T. Hayashi, S. Hengrasme, Y. Matsumoto, *Chem. Lett.* **1990**, 1377; T. Hayashi, Y. Matsumoto, I. Morikawa, Y. Ito *Tetrahedron Asymmetry* **1990**, 1, 151.
- [11] M. Sawamura, H. Hamashima, Y. Ito, *J. Am. Chem. Soc.* **1992**, 114, 8295.
- [12] S. Nukui, M. Sodeoka, M. Shibasaki, *Tetrahedron Lett.* **1993**, 34, 4965.
- [13] M. Watanabe, S. Araki, Y. Butsugan, M. Uemura, *Chem. Express* **1989**, 4, 825; M. Watanabe, S. Araki, Y. Butsugan, M. Uemura, *ibid.* **1990**, 5, 661; M. Watanabe, N. Hashimoto, S. Araki, Y. Butsugan, *J. Org. Chem.* **1992**, 57, 742; M. Watanabe, S. Araki, Y. Butsugan, *ibid.* **1991**, 56, 2218; M. Watanabe, M. Komota, M. Nishimura, S. Araki, Y. Butsugan, *J. Chem. Soc., Perkin Trans. 1* **1993**, 2193; H. Wally, M. Widhalm, W. Weissensteiner, K. Schlögl, *Tetrahedron Asymmetry* **1993**, 4, 285.
- [14] A. W. Burgstahler, D. L. Boger, N. C. Naik, *Tetrahedron* **1976**, 32, 309.
- [15] R. L. Halterman, K. P. C. Vollhardt, *Organometallics* **1988**, 7, 883.
- [16] R. L. Halterman, K. P. C. Vollhardt, *Tetrahedron Lett.* **1986**, 27, 1461.
- [17] L. A. Paquette, K. J. Moriarty, J. A. McKinney, R. D. Rogers, *Organometallics* **1989**, 8, 1707.
- [18] M. L. McLaughlin, J. A. McKinney, L. A. Paquette, *Tetrahedron Lett.* **1986**, 27, 5595.
- [19] L. A. Paquette, J. A. McKinney, M. L. McLaughlin, A. L. Rheingold, *Tetrahedron Lett.* **1986**, 27, 5599.
- [20] R. B. Grossman, J. C. Tsai, W. M. Davis, A. Gutiérrez, S. L. Buchwald, *Organometallics* **1994**, 13, 3892.
- [21] R. L. Halterman, K. P. C. Vollhardt, M. E. Welker, *J. Am. Chem. Soc.* **1987**, 109, 8105; Z. Chen, K. Eriks, R. L. Halterman, *Organometallics* **1991**, 10, 3449; Z. Chen, R. L. Halterman, *Synlett* **1990**, 103; S. L. Colletti, R. L. Halterman, *Tetrahedron Lett.* **1989**, 30, 3513; S. L. Colletti, R. L. Halterman, *Organometallics* **1991**, 10, 3438.
- [22] G. Erker, A. A. H. van der Zeijden, *Angew. Chem.* **1990**, 102, 543; G. Erker, *J. Organomet. Chem.* **1990**, 400, 185; G. Erker, *Pure Appl. Chem.* **1991**, 63, 797; R. L. Halterman, A. Tretyakov, *Tetrahedron* **1995**, 51, 4371.
- [23] M. L. H. Green, N. M. Walker, *J. Organomet. Chem.* **1988**, 344, 379; J. A. Bandy, M. L. H. Green, I. M. Gardiner, K. Prout, *J. Chem. Soc., Dalton Trans.* **1991**, 2207.
- [24] P. Vedso, R. Chauvin, Z. Li, B. Bernet, A. Vasella, *Helv. Chim. Acta* **1994**, 77, 1631.
- [25] G. W. J. Fleet, J. C. Son, D. S. C. Green, I. Cenci di Bello, *Tetrahedron* **1988**, 44, 2649.
- [26] V. A. Mironov, A. P. Ivanov, Y. M. Kimelfeld, L. I. Petrovskaya, A. A. Akhrem, *Tetrahedron Lett.* **1969**, 3347; L. M. Dané, J. W. de Haan, H. Kloosterziel, *ibid.* **1970**, 2755; M. F. Semmelhack, H. N. Weller, J. S. Foos, *J. Am. Chem. Soc.* **1977**, 99, 292; K. S. Replogle, B. K. Carpenter, *J. Am. Chem. Soc.* **1984**, 106, 5751.
- [27] J. C. Irvine, W. Burt, *J. Chem. Soc.* **1924**, 1343; W. N. Haworth, E. L. Hirst, J. I. Webb, *ibid.* **1930**, 651.
- [28] H. B. Sinclair, *Carbohydr. Res.* **1970**, 12, 150.
- [29] T. K. M. Shing, *Tetrahedron* **1988**, 44, 7261.
- [30] A. Duréault, M. Portal, J. C. Depezay, *Synlett* **1991**, 225.
- [31] R. W. Fish, M. Rosenblum, *J. Org. Chem.* **1965**, 30, 1253; D. W. Slocum, T. R. Engelmann, *J. Organomet. Chem.* **1970**, 24, 753; M. Rausch, M. Vogel, H. Rosenberg, *J. Org. Chem.* **1957**, 22, 900; D. W. Slocum, B. P. Koonsvitsky, *ibid.* **1976**, 41, 3664.