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Enantiomerically pure C_2-symmetric bridged ferrocene and titanocene derivatives

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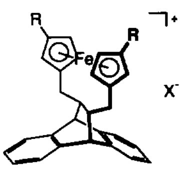
Abstract

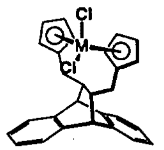
The chiral ansa metallocenes *trans*-(11*R*,12*R*)-bis-(η^5-cyclopentadienylmethyl)-dibenzobicyclo-[2.2.2]octano-iron(II) (**6**) and *trans*-(11*R*,12*R*)-bis-(η^5-cyclopentadienylmethyl)dibenzobicyclo-[2.2.2]-octano-titanium(IV) dichloride (**8**) have been prepared from the dilithium salt of *trans*-(11*R*,12*R*)-bis-(cyclopentadienyl-methyl)-9,10-dihydro-9,10-ethanoanthracene (**4**) by reaction with $FeCl_2$ and $TiCl_4$, respectively. Oxidation of the ferrocene derivative (**6**) with $NOBF_4$ gave *trans*-(11*R*,12*R*)-bis-(η^5-cyclopentadienylmethyl)-dibenzo-bicyclo-[2.2.2]octano-iron(III) tetrafluoroborate (**7**) which catalyzes the Diels–Alder reaction of methacrylaldehyde with cyclopentadiene giving high diastereo- but modest enantio-selectivity.

1. Introduction

A wide variety of metallocenes with a C_1-, SiR_2- or C_2-bridge connecting two cyclopentadienyl groups have been prepared. In particular, titano- and zircono-cenes of this type have been intensely studied after Brintzinger and Kaminsky [1] demonstrated their usefulness as Ziegler–Natta catalysts. In contrast, only a few C_3- or C_4-bridged metallocenes are known. Very recently Lang and Seifert [2] reported the syntheses of titano- and zircono-cenes bridged by a $SiMe_2CH_2$-CH_2SiMe_2 connector. Here we report the syntheses of a ferrocene and a titanocene with cyclopentadienyl groups bridged by a chiral C_4 connector unit.



A



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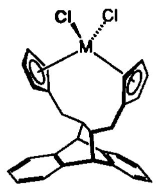

C

Our interest in chiral ferrocenes arose from a recent report by Kelly and Chandrakumar [3] in which ferricenium hexafluorophosphate was shown to be a weak Lewis acid capable of catalyzing Diels–Alder reactions of α,β-unsaturated carbonyl compounds. A chiral ferricenium salt, therefore, appeared to be of interest as a catalyst for organic synthesis. Model considerations indicated that a ferricenium salt of type **A** ($R \neq H$) would be a highly discriminating monodendate chiral Lewis acid, allowing the arrangement of nearly parallel cyclopentadienyl planes at a distance of *ca.* 3.4 Å, which comes close to the value found for ferrocene (3.32 Å). However, a report by Lüttringhaus and Kullick [4] on a synthesis of the $(CH_2)_4$-bridged ferrocene, from 1,4-biscyclopentadienylbutane via reaction of the dianion with $FeCl_2$, which gave a yield as low as 0.05%, was somewhat discouraging. It occurred to us that the dianion of the biscyclopentadienyl derivative **4** (Scheme 1) might, due to steric effects, have a conformation resembling that of the product and thus allow the ring closure in reasonable yield.

Having accomplished the above goal, we asked ourselves whether the basic system would allow the construction of a tetrahedral metallocene. Models indi-

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cated that a compound of type **B**, in which the C_2-symmetry of the chiral backbone is broken, would be feasible. In **B** the ligands on M are diastereotopic and might be stereoselectively substituted. However, models also indicated that there is a C_2-symmetric conformation **C** which appeared somewhat strained but nevertheless possible. These ideas were a sufficient inducement for us to attempt the syntheses of the corresponding titanocene and zirconocene **B** and **C**, with M = Ti and Zr, respectively.

2. Results and discussion

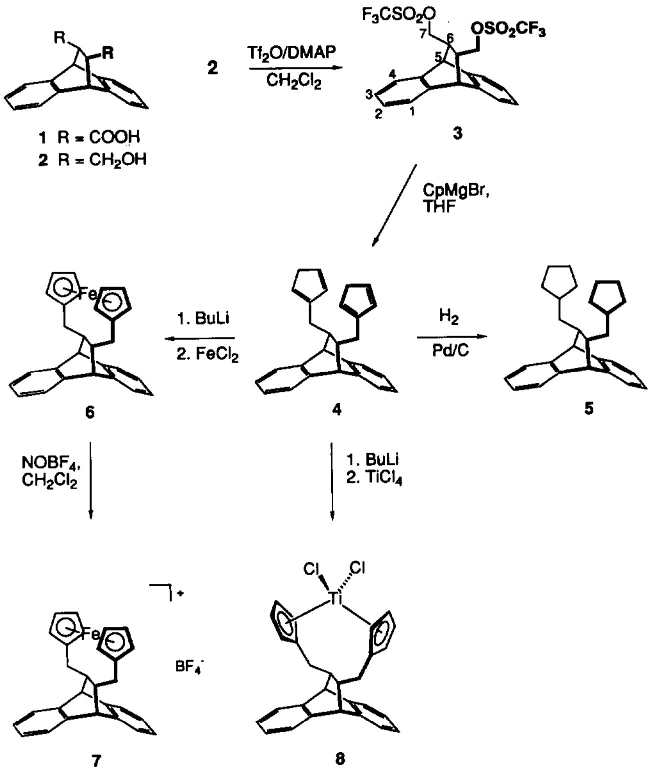
The dicarboxylic acid **1** (Scheme 1), serving as the chiral basis in the present work, can be readily prepared enantiomerically pure and on a 100 g scale by an asymmetric Diels–Alder reaction of bis-[(*S*)-1-ethoxycarbonylethyl]-fumarate with anthracene and subsequent saponification [5]. Reduction of **1** with lithium aluminium hydride (LAH) gave the known [6] diol **2** in 95% yield.

For the preparation of the biscyclopentadienyl derivative **4** by nucleophilic displacement reactions, various derivatives of **2** and various cyclopentadienyl metal compounds were investigated. The tosylate [6] and the iodide [6] reacted sluggishly, but the triflate **3** was sufficiently reactive. This compound (crystalline) was obtained from **2** by reaction with trifluoromethanesulfonic anhydride (Tf_2O) in the presence of *N*,*N*-(dimethylamino)pyridine (DMAP) as a catalyst in 93% yield. The nucleophiles CpLi, CpNa and CpMgBr [7] were investigated and the latter proved most suitable. In contrast to CpLi and CpNa, this compound can be prepared easily and stored for extended periods of time, and the reaction with **3** was complete within 15 min in THF at −78°C to give the crystalline biscyclopentadiene derivative **4** in 91% yield. Immediately after work-up, **4** displayed a single set of NMR signals. After a few hours at room temperature, hydrogen migration was apparent. Additional signals in the olefin region of the spectrum indicated the formation of the other two diene isomers. In solution, **4** slowly oligomerizes (*ca.* 50% conversion after 72 h at room temperature) by a Diels–Alder reaction. For unambiguous characterization, **4** was transformed into the saturated compound **5** by catalytic hydrogenation (yield 98%).

TABLE 1. Experimental crystallographic data for **6** [a]

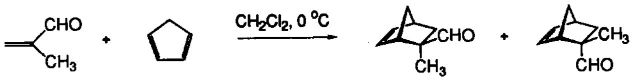
Formula	$C_{28}H_{24}Fe$
F.W.	416.35
Space group	$P2_1$ (No. 4)
Temperature (°C)	25
Crystal system	Monoclinic
Cell constants	
a (Å)	16.177 (5)
b (Å)	15.527 (6)
c (Å)	17.003 (6)
β (°)	104.83 (3)
Z	8
Cell volume (Å^3)	4128.5
Diffractometer	Siemens (Nicolet) R3
Radiation, graphite monochromator	Mo Kα
2θ range	$2° \leq 2\theta \leq 50°$
Scan-speed	$2.3° \leq \omega \leq 29.3°$ min^{-1}
Reflections measured	7625
Independent reflections	5501
No. of parameters varied	596
Computer program	SHELXTL-PLUS [11]
R_1	0.0699
R_2	0.0557

[a] Carbon atoms in the phenyl or cyclopentadienyl rings were refined isotropically, and other carbon atoms and Fe anisotropically. Hydrogen atoms were placed in calculated positions.



Scheme 1.

The ferrocenophane **6** was obtained in 60% yield by reaction of **4** with 2 equiv. of n-butyllithium in THF and subsequent addition of $FeCl_2$. The crystalline, yellow compound **6** was characterized by NMR spectroscopy, microanalysis and an X-ray crystal structure determination (Tables 1, 2 and 3). The X-ray data (*cf.* Fig. 1) clearly demonstrate that the ferrocene nucleus fits into the chiral C_2-symmetric framework without strain.



Oxidation of the ferrocenophane **6** with $NOBF_4$ in CH_2Cl_2 gave the blue crystalline ferricenium salt **7** in 95% yield. Its catalytic activity was tested in the Diels–Alder reaction of methacrylaldehyde with cyclopentadiene. The diastereoselectivity (ratio of exo to endo Diels–Alder adduct) was determined by GLC. For assessment of enantioselectivity of the exo adduct, Yamamoto's procedure [8] was used involving acetalization of the crude product with (2*R*,4*R*)-2,4-pentanediol followed by GLC analysis of the resulting diastereomeric acetals. Comparison with the non-catalyzed reaction (Table 4) indicated an approximate 13-fold rate enhancement and a very pronounced enhancement of the exo to endo ratio. As expected, enantioselectivity (55:45) was low because of a low degree of chiral discrimination of the tilted C–H bonds at the assumed binding site (**A**, R = H). An effort is being made to synthesize other compounds of type **A** with R a group other than H.

TABLE 2. Selected bond lengths (pm) and bond angles (°) in **6**

Fe–C(1)	204.0(6)	C(6)–C(14)	148.2(10)
Fe–C(2)	205.2(6)	C(11)–C(12)	155.9(10)
Fe–C(3)	205.5(6)	C(12)–C(13)	156.3(12)
Fe–C(4)	204.6(6)	C(12)–C(15)	157.6(13)
Fe–C(5)	203.6(7)	C(13)–C(18)	150.4(13)
Fe–C(6)	204.0(6)	C(13)–C(28)	151.6(11)
Fe–C(7)	205.1(6)	C(14)–C(15)	154.0(13)
Fe–C(8)	205.4(6)	C(15)–C(16)	155.3(12)
Fe–C(9)	204.5(6)	C(16)–C(17)	150.4(14)
Fe–C(10)	203.7(6)	C(16)–C(23)	151.8(12)
C(1)–C(2)	142.0(1)	C(17)–C(18)	139.8(14)
C(1)–C(5)	142.0(1)	C(17)–C(22)	138.4(14)
C(1)–C(11)	150.7(11)	C(18)–C(19)	139.0(14)
C(2)–C(3)	142.0(1)	C(19)–C(20)	138.3(15)
C(3)–C(4)	142.0(1)	C(20)–C(21)	133.7(18)
C(4)–C(5)	142.0(1)	C(21)–C(22)	139.3(15)
		C(12)–C(13)–C(18)	109.2(7)
C(1)–Fe–C(5)	40.8(1)	C(12)–C(13)–C(28)	104.4(7)
C(1)–Fe–C(6)	108.5(2)	C(14)–C(15)–C(12)	108.4(7)
C(1)–Fe–C(7)	133.2(2)	C(14)–C(15)–C(16)	113.0(7)
C(1)–Fe–C(8)	173.0(2)	C(15)–C(16)–C(23)	106.9(7)
C(1)–Fe–C(9)	145.1(2)	C(15)–C(16)–C(17)	107.1(7)
C(1)–Fe–C(10)	113.7(2)	C(17)–C(16)–C(23)	107.9(8)
C(1)–C(11)–C(12)	40.7(1)	C(17)–C(18)–C(13)	113.6(8)
C(4)–Fe–C(5)	108.0(0)	C(18)–C(13)–C(28)	107.0(7)
C(5)–C(1)–C(2)	113.9(7)	C(18)–C(17)–C(16)	112.4(9)
C(6)–C(14)–C(15)	116.3(6)	C(23)–C(28)–C(13)	113.2(7)
C(11)–C(12)–C(15)	113.6(6)	C(28)–C(23)–C(16)	113.1(8)
C(11)–C(12)–C(13)	110.2(7)		

TABLE 3. Atom positional parameters ($\times 10^4$) with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

	x	y	z	U
Fe(1)	2986(1)	5285(1)	8413(1)	44(1)
C(1)	3824(4)	4529(3)	8010(4)	38(2)
C(2)	3067(4)	4651(3)	7377(4)	43(2)
C(3)	2962(4)	5549(3)	7223(4)	62(3)
C(4)	3654(4)	5982(3)	7759(4)	62(3)
C(5)	4187(4)	5352(3)	8245(4)	53(3)
C(6)	2982(3)	4899(4)	9560(3)	41(2)
C(7)	3008(3)	5812(4)	9524(3)	58(3)
C(8)	2270(3)	6093(4)	8930(3)	76(3)
C(9)	1788(3)	5355(4)	8600(3)	66(3)
C(10)	2229(3)	4616(4)	8989(3)	57(3)
C(11)	4187(6)	3665(6)	8223(5)	50(4)
C(12)	4572(5)	3635(6)	9262(5)	39(3)
C(13)	5237(5)	2887(5)	9491(5)	41(3)
C(14)	3616(6)	4347(6)	10122(5)	50(4)
C(15)	3881(5)	3514(6)	9759(5)	40(3)
C(16)	4193(6)	2798(6)	10404(5)	55(4)
C(17)	4233(6)	1975(7)	9950(5)	53(2)
C(18)	4770(5)	2042(6)	9426(5)	48(2)
C(19)	4810(6)	1367(6)	8901(6)	55(3)
C(20)	4339(7)	626(7)	8916(7)	79(4)
C(21)	3843(7)	566(7)	9434(7)	78(4)
C(22)	3762(6)	1233(6)	9957(6)	62(3)
C(23)	5098(6)	3032(6)	10866(6)	50(3)
C(24)	5380(7)	3228(7)	11690(7)	74(3)
C(25)	6245(7)	3439(7)	12005(7)	79(3)
C(26)	6795(7)	3402(7)	11531(7)	73(3)
C(27)	6541(6)	3212(6)	10707(6)	65(3)
C(28)	5665(6)	3028(6)	10384(5)	48(2)

Preparation of the titanocene **8** proved to be difficult. Under a variety of reaction conditions the dilithium salt of **4** with $TiCl_4$ gave mixtures of the target compound **8**, along with oligomers that displayed varying solubility properties depending on the reaction conditions. At high concentrations of the reactants, relatively insoluble by-products were formed and the monomer **8** was isolated by extraction with toluene and purified by recrystallization (yield 13%). Titanocene **8** forms red microcrystals and was unambiguously characterized by spectroscopic data and molecular weight determination (vapor pressure osmometry). NMR spectra (solvent $CDCl_3$) indicated a C_2-symmetric structure. Preparation of the corresponding zirconocene (**B**, **C**: M = Zr) was attempted but has not been accomplished to date.

3. Experimental details

3.1. General comments

3.1.1. *Instrumentation*

NMR spectra were recorded on a Bruker WH 300 instrument at 303 K in $CDCl_3$. Spectra were obtained at the following frequencies: 300.133 MHz (^{1}H), 75.46 MHz (^{13}C). For numbering of atoms, see the formula for **3**. Melting points were determined on a Büchi melting point apparatus (Dr. Tottoli) and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 instrument; $[\alpha]_D$ was extrapolated from $[\alpha]_{578}$ and $[\alpha]_{546}$ with the Drude equation. Preparative medium pressure chromatography (MPLC) was performed with silica columns (40 × 4 cm^2, Kieselgel Merck LiChroprep Si 60, 20 lm, 10000 theoretical plates), packed according to the procedure of Helmchen and Glatz [9]; detection, Knauer UV/VIS Filter-photometer (254). The mass spectrum of compound **8** was recorded on a Varian MAT 711 (SS 100) at 20 eV and 438 K. The molecular weight of compound **8** was determined on a Knauer Dampfdruck osmometer.

TABLE 4. Diels–Alder reaction (CH_2Cl_2, 0°C, 3 h) of methacrylaldehyde (c = 0.15 mol l^{-1}) with cyclopentadiene (10 equiv.)

Catalyst	Yield (%)	exo/endo ratio	ee (%)
7 (0.5 equiv.)	69	99: 1	10
–	7	86:14	–

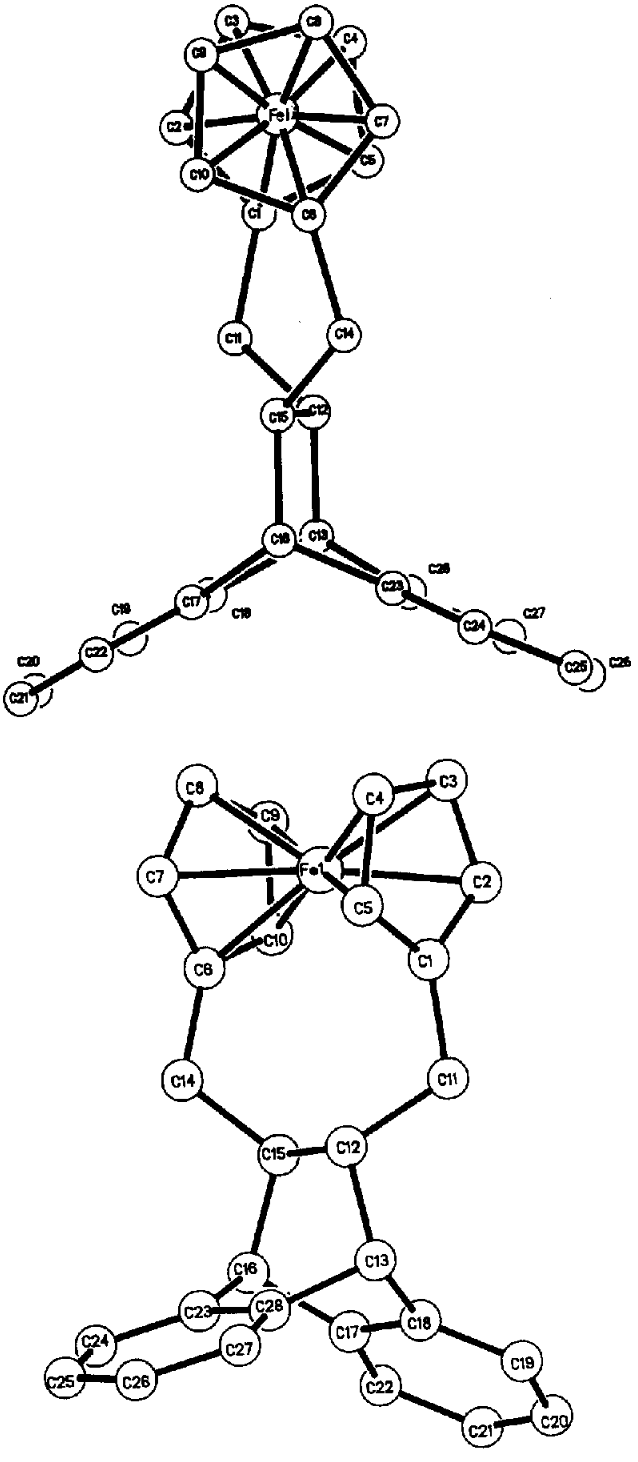


Fig. 1. Molecular structure of compound **6** in two different perspectives.

3.1.2. Methods

All reactions were carried out under argon by using standard Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl and dichloromethane was dried and distilled from CaH_2 and then stored over molecular sieves. Chloroform was filtered through alumina (neutral, activity 1), degassed by ultrasound, and saturated with argon. The optical rotation of the diol **2** was $[\alpha]_D^{22} = -13.1$, $[\alpha]_{578}^{22} = -13.8$ (c = 0.9, 95% EtOH); Lit. [6] $[\alpha]_{578}^{22} = -13.8$ (c = 1, EtOH). Trifluoromethanesulfonic anhydride was freshly distilled before use. Cyclopentadienylmagnesium bromide (CpMgBr) was prepared by a published procedure [7] and stored under argon at 4°C. Anhydrous $FeCl_2$ was prepared by the procedure described by King [10].

3.2. *trans-(R,R)-Bis-[(trifluoromethylsulfonyl)oxymethyl]9,10-dihydro-9,10-ethanoanthracene (3)*

A solution of 1.00 g (3.75 mmol) of diol **2** and 1.10 g (9.00 mmol) of DMAP in 15 ml of $CHCl_3$ was added dropwise to a cooled (0°C) solution of 2.33 g (8.26 mmol) of trifluoromethanesulfonic anhydride in 5 ml of $CHCl_3$. After 2.5 h at 0–5°C, a precipitate had formed and the mixture was filtered through a pad of silica gel (4 × 3 cm^2, eluent $CHCl_3$). The filtrate was concentrated *in vacuo* at room temperature to give 1.85 g (93%) of a colorless crystal powder, m.p. 131–132°C, which could be stored at 4°C for several months. Optical rotation: $[\alpha]_D^{20} = +6.8$, $[\alpha]_{578}^{20} = +7.0$, $[\alpha]_{546}^{20} = +7.5$, $[\alpha]_{436}^{20} = +12.3$, $[\alpha]_{365}^{20} = +17.5$ (c = 1, CH_2Cl_2). ^{1}H

NMR: δ 1.88–1.93 (m, 2H, 6-H); 4.00 (dd, 2H, 7-Ha $^3J = 5.4$ Hz); 4.20 (dd, 2H, 7-H_b, $^2J = 10.0$ Hz, $^3J = 9.6$ Hz), 4.38 (bs, 2h, 5-H); 7.20–7.39 (m, 8H, aromat.) ppm. ^{13}C NMR: δ 141.40, 138.50 (s, aromat.); 127.25, 126.91, 125.71, 124.09 (d, aromat.); 124.92, 120.68, 116.45, 112.21 (CF_3); 77.13 (t, C-7); 44.59, 42.40 (d, C-5, C-6) ppm. Anal. Found: C, 45.35; H, 3.33. $C_{20}H_{16}O_6F_6S_2$ calc.: C, 45.28; H, 3.04%.

3.3. *trans-(R,R)-Bis-(cyclopentadienylmethyl)-9,10-dihydro-9,10-ethanoanthracene (4)*

A solution of 1.00 g (1.88 mmol) of **3** in 5 ml of THF was added dropwise to a stirred solution of 4.0 g (80 mmol) of CpMgBr · *n*(THF) in 10 ml of THF at −78°C. After 15 min stirring at −78°C, 50 ml of n-hexane were added. Filtration of the colorless suspension through a pad of silica (3 × 3 cm, eluent n-hexane) and evaporation of the solvent (room temperature) yielded 0.62 g (91%) of **4** as a colorless powder. This material was used in subsequent steps without further purification. Recrystallization from n-hexane afforded colorless needles, m.p. 116–118°C. Compound **4** could be stored as a solid at −20°C for 2 weeks without noticeable decomposition. However, a solution of **4** in $CDCl_3$ at room temperature showed a considerable degree of polymerization (Diels–Alder reaction) over a period of 24 h (NMR monitoring). ^{1}H NMR: δ 1.73 (bs, 2H, 6-H); 2.16–2.24 (m, 4H, 7-H); 2.92–3.15 (q, 4H, CH_2[Cp]); 4.21 (s, 2H, 5-H); 6.38–6.65 (m, 6H, Cp); 7.26–7.40 (m, 8H, aromat.) ppm. ^{13}C NMR: δ 147.65, 144.35, 140.94 (s, aromat., Cp); 132.43, 130.97, 128.30, 125.73, 125.64, 125.37, 123.05 (d, aromat., Cp); 48.01, 47.05 (d, C-5, C-6); 43.18 (t, Cp); 36.23 (t, C-7) ppm.

3.4. *trans-(R,R)-Bis-(cyclopentylmethyl)-9,10-dihydro-9,10-ethanoanthracene (5)*

A solution of 0.60 g (1.65 mmol) of **4** in 150 ml of *n*-hexane was treated with 0.10 g Pd/C (10%) and stirred under hydrogen first for 2 h at room temperature and then for 2 h at 55°C. Filtration through Celite and evaporation of the solvent gave 0.62 g (98%) of **5** as a colorless oil. Optical rotation: $[\alpha]_D^{20} = -15.2$, $[\alpha]_{578}^{20} = -16.1$, $[\alpha]_{546}^{20} = -18.9$, $[\alpha]_{436}^{20} = -38.2$, $[\alpha]_{365}^{20} = -72.2$ ($c = 1.3$, *n*-hexane). ^{1}H NMR: δ 0.96–1.06 (m, 8H, cyclopentyl); 1.27–1.34 (m, 2H, 6-H); 1.48–1.64 (m, 8H, cyclopentyl); 1.68–1.76 (m, 4H, 7-H_a, cyclopentyl); 1.89–2.02 (m, 2H, 7-H_b); 4.07 (d, 2H, 5-H, $^3J = 1.05$ Hz); 7.09–7.26 (m, 8H, aromat.) ppm. ^{13}C NMR: δ 144.40, 141.41 (s, aromat.); 125.53, 125.28, 125.20, 122.97 (d, aromat.); 48.51, 45.69, 37.82 (d, C-5, C-6, cyclopentyl); 42.00 (t, C-7); 33.30, 32.55, 25.14, 25.11 (t, cyclopentyl) ppm. Anal. Found: C, 90.79; H, 9.34. $C_{28}H_{34}$ calc.: C, 90.75; H: 9.25%.

3.5. *trans-(R,R)-Bis-(η^5-cyclopentadienylmethyl)-dibenzobicyclo-[2.2.2]octano-iron(II) (6)*

To a solution of 0.95 g (2.62 mmol) of **4** in 10 ml of THF at −78°C was added dropwise 5.24 mmol of n-butyllithium (1.6 M solution in hexane). After 20 min stirring at −78°C, the mixture was allowed to warm to room temperature and stirring was continued for 4 h. The clear solution was treated with a suspension of 0.35 g (2.80 mmol) of $FeCl_2$ in 10 ml of THF during 15 min. After 3 h stirring at room temperature, the mixture was filtered through Celite and the filtrate concentrated *in vacuo*. The yellow residue was extracted with boiling n-hexane and the extract concentrated to give 0.88 g (81%) of a yellow powder. Purification by MPLC [l.b. petroleum ether (35–70°C), $F = 35$ ml/min, $t_R = 56$ min] furnished 0.65 g (60%) of **6**. Recrystallization from ethanol gave well formed yellow monoclinic crystals, m.p. 184–185°C. Optical rotation: $[\alpha]_D^{20} = +115.0$, $[\alpha]_{578}^{20} = +117.4$, $[\alpha]_{546}^{20} = +127.5$, $[\alpha]_{436}^{20} = +35.0$, $[\alpha]_{365}^{20} = +87.8$ ($c = 1$, $CHCl_3$). ^{1}H NMR: δ 1.45 (dd, 2H, 7-H_a, $^3J = 11.2$ Hz); 2.05–2.09 (m, 2H, 6-H); 2.57 (d, 2H, 7-H_b, $^2J = 13.7$ Hz, $^3J = 0$ Hz); 4.08 (bs, 2H, 5-H); 3.87–4.15 (m, 8H, Cp); 7.09–7.37 (m, aromat.) ppm. ^{13}C NMR: δ 143.73, 141.01 (s, aromat.); 125.71, 125.44, 124.78, 123.26 (d, aromat.); 89.20 (s, Cp); 71.07, 68.09, 67.63, 66.42 (d, Cp); 51.91, 48.25 (d, C-5, C-6); 37.57 (t, C-7). Anal. Found: C, 80.59; H, 6.00. $C_{28}H_{24}Fe$ calc.: C, 80.78; H, 5.81%.

3.6. *trans-(R,R)-Bis-(η^5)-cyclopentadienylmethyl)-dibenzobicyclo-[2.2.2]-octano-iron(III) tetrafluoroborate (7)*

Argon was bubbled through a solution of 70 mg (0.60 mmol) of $NOBF_4$ in 10 ml of CH_2Cl_2 and a solution of 250 mg (0.60 mmol) of **6** in 5 ml of CH_2Cl_2 was added. The mixture turned blue immediately. After 30 min stirring at room temperature, the mixture was filtered and the filtrate concentrated *in vacuo*. The blue solid residue was washed with water, ethanol, and ether and dried *in vacuo*. Yield: 286 mg (95%) of a blue powder, m.p. 113–115°C (decomp.). Anal. Found: C, 67.08; H, 4.90. $C_{28}H_{24}FeBF_4$ calc.: C, 66.84; H, 4.81%.

3.7. *trans-(R,R)-Bis-(η^5-cyclopentadienylmethyl)-dibenzobicyclo-[2.2.2]-octano-titanium(IV) dichloride (8)*

A solution of the dilithium salt of **4** was prepared as described above from 0.60 g (1.65 mmol) of **4** and 3.32 mmol of *n*-butyllithium in 4 ml of THF at 0°C. Then a solution of 0.31 g (1.65 mmol) of $TiCl_4$ in 4 ml of toluene was added. The mixture slowly turned red. After 2 h stirring at room temperature, the solvents were evaporated *in vacuo* (0.1 Torr) and the resulting black residue was extracted with CH_2Cl_2 and the extract filtered. The extract was concentrated at reduced pressure to a volume of 4 ml and treated with 4 ml of toluene cooled to −20°C, whereupon 103 mg (13%) of **8** separated as air-stable red crystals that contained toluene. Recrystallization, resulting in some loss of material, from CH_2Cl_2/ether gave toluene-free red crystals, m.p. 151–153°C (decomp.). ^1H NMR: δ 1.89–1.92 (m, 2H, 6-H); 2.16 (dd, 2H, 7-H_a, $^3J = 9.6$ Hz); 2.90 (d, 2H, 7-H_b, $^2J = 16$ Hz, $^3J = 0$ Hz); 4.05 (bs, 2H, 5-H); 6.24–6.77 (m, 8H, Cp); 7.10–7.32 (m, aromat.). MS: *m/e* 482 (1.47%), 481 (2.17%), 480 (5.25%), 479 (2.66%), 478 (7.37%), 445 (1.35%), 444 (1.40%), 443 (3.19%), 442 (1.30%), 268 (1.78%), 267 (7.59%), 266 (6.33%), 265 (20.62%), 264 (6.04%), 263 (2.58%), 230 (1.51%), 229 (5.54%), 228 (7.54%), 227 (1.77%), 200 (1.39%), 179 (16.76%), 178 (100%), 36 (1.63%). Molecular weight determination (vapor pressure osmometry, CH_2Cl_2), calc.: 479.3; found: 477. Anal. Found: C, 69.29; H, 5.24. $C_{28}H_{24}TiCl_2$ calc.: C, 70.16; H, 5.05%.

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