ELSEVIER

Journal of Chromatography A, 973 (2002) 115–122

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Separation of planar chiral ferrocene derivatives on β-cyclodextrin-based polymer supports prepared via ring-opening metathesis graft-polymerization

Betina Mayr[a], Herwig Schottenberger[b], Olaf Elsner[b], Michael R. Buchmeiser[a,*]

[a]*Institute of Analytical Chemistry and Radiochemistry, University of Innsbruck, Innrain 52 a, A-6020 Innsbruck, Austria*

[b]*Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52 a, A-6020 Innsbruck, Austria*

Received 15 March 2002; received in revised form 19 June 2002; accepted 5 August 2002

Abstract

A series of β-cyclodextrin (β-CD) based chiral stationary phases (CSPs) were synthesized by ring-opening metathesis graft polymerization of various norborn-2-ene (NBE) substituted CDs. Chiral selectors based on *endo*/*exo*-6-*O*-(norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tris(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tetrakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, hexakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD and tetrakis(*endo*-6-*O*-norborn-2-ene-5-carboxyl)-β-CD were grafted onto Nucleosil 300-5 using well-established grafting procedures. CSPs were investigated for their separation capabilities for a series of the planar chiral ferrocene derivatives, *rac*-ferroceno[2,3*a*]inden-1-one (**1a**, **1b**), *rac*-6-(3-hydroxy-3-methylbut-1-yn-1-yl)ferroceno[2,3*a*]inden-1-one (**2a**, **2b**), *rac*-ferrocene[2,3*a*]indene (**3a**, **3b**), *rac-endo* 1-methoxy-1-allylferroceno[2,3*a*]indene (**4a**, **4b**) and *rac*-1,4-dihydroxybutylferrocene (**5a**, **5b**). Compounds **1a**, **1b** and **2a**, **2b** bearing a carbonyl group were successfully separated on these CSPs, while compounds **3**–**5** do not undergo enantioselective interaction under the conditions applied. General aspects of separation as well as mechanistic implementations are discussed.

Keywords: Chiral stationary phases, LC; Ring-opening metathesis polymerization; Metallocenes, planar chiral

1. Introduction

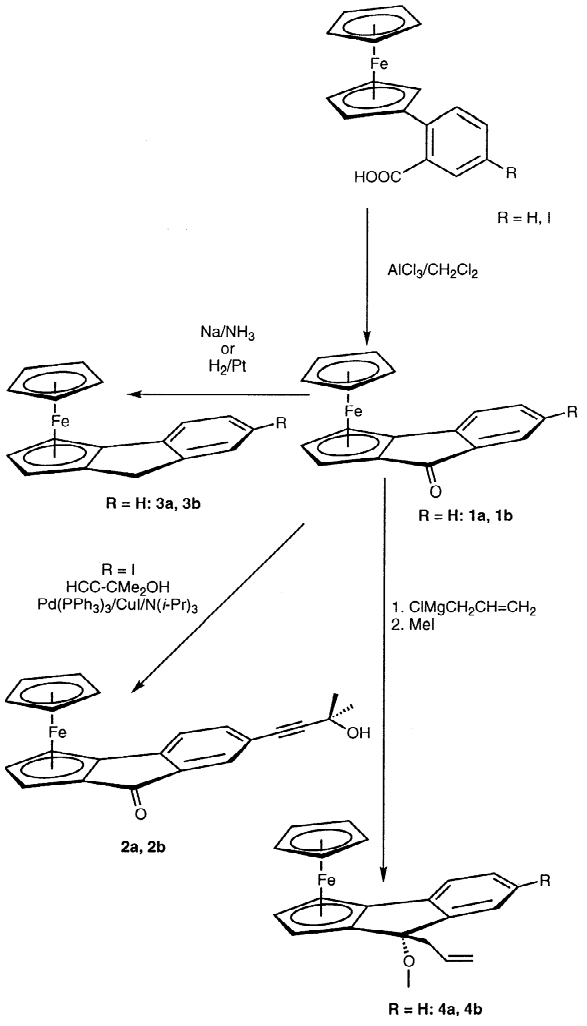
Planar chiral ferrocenes are important ligands in the area of homogeneous asymmetric catalysis [1]. While chiral diphosphinoferrocenes such as those of the Josiphos, Taniaphos, MandyPhos and BoPhoz type have successfully been used in many enantioselective reactions [2–5], planar chiral ferroceno[2,3*a*]indenes have found application as ligands in stereoselective metallocene-catalyzed olefin polymerization [6]. The synthetic route to this type of ligands entails an intramolecular Diels–Alder acylation of 2-ferrocenylbenzoic chloride with $AlCl_3$. This desired target molecule, ferroceno[2,3*a*]inden-1-one (**1**), is obtained as a racemate of **1a** and **1b** (Scheme 1).

In analogy, the corresponding 6-iodo-derivative is accessible starting from 5-iodo-2-ferrocenylbenzoic acid. Sonogashira–Hagihara coupling with 3-hy-

*Corresponding author. Tel.: +43-512-507-5184; fax: +43-512-507-2677.

E-mail address: michael.r.buchmeiser@uibk.ac.at (M.R. Buchmeiser).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01197-4



Scheme 1. Synthesis of racemic compounds **1**–**4**.

droxy-3-methylbut-1-yne yields *rac*-6-(3-hydroxy-3-methylbut-1-yn-1-yl)ferroceno[2,3*a*]inden-1-one (**2a**, **2b**). Using either sodium in liquid ammonia or carbon-immobilized platinum/hydrogen, the parent racemate (**1a**, **1b**) can be reduced to *rac*-ferrocene[2,3*a*]indene (**3a**, **3b**). Alternatively, reaction of (**2a**, **2b**) with allylmagnesium bromide followed by addition of methyl iodide yields two sets of enantiomers, *rac-exo* and *endo* 1-methoxy-1-allyl-ferroceno[2,3*a*]indene (**4a**, **4b**) which can be separated into the two sets of enantiomers by chromatography on silica using diethyl ether–*n*-pentane as an eluent. In order to obtain enantiomerically pure ligands and in due consequence enantiomerically pure catalysts (Fig. 1), the separation of these ferroceno[2,3*a*]indenes needed to be accomplished.

Among the vast number of enantioselective columns available [7,8], β-cyclodextrin (β-CD) based chiral stationary phases (CSPs) were chosen for two reasons. On the one hand, both suitable selectors and supports have been prepared and successfully used in our group for the separation of various chiral compounds including β-blockers as well as dansyl-, 3,5-dinitrobenzoyl- and FMOC-protected amino acids [9,10]. On the other hand, with this synthetic repertoire available, any successful separation can be upscaled to obtain the desired quantity of compounds. In order to reduce costs to a minimum, this is again best accomplished with ''laboratory-made''

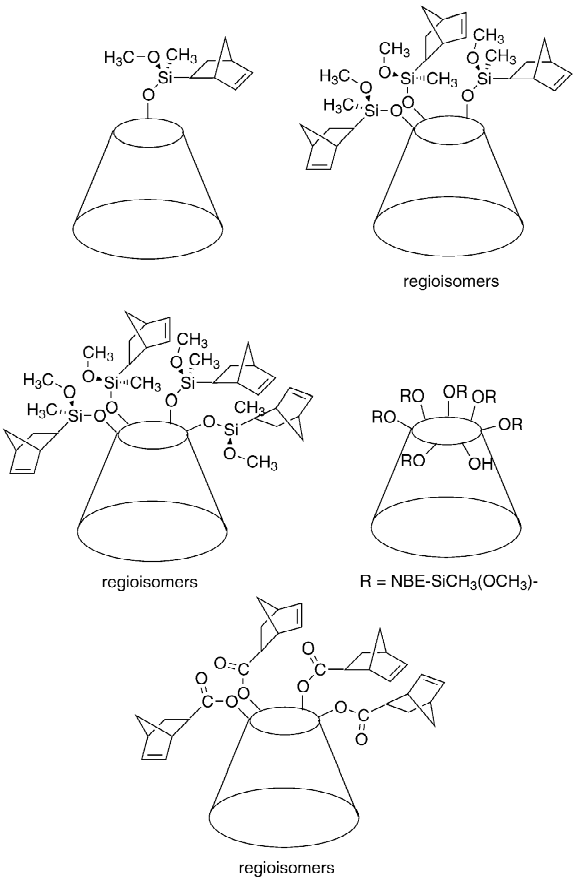


Fig. 1. Structures of chiral ferrocene derivatives **1**–**5** and example of a Zr-based metallocene (**6**) prepared from enantiomerically pure dimethylsilylene-bridged **3a**.

systems. In the following, we report on the successful separation of planar chiral ferrocenes by β-CD-based supports prepared by ring-opening metathesis graft-polymerization.

2. Experimental

General experimental details and instrumentation are described elsewhere [12]. Nucleosil 300-5 (5 μm, 300 Å, σ=100 m^2) was purchased from Merck (Darmstadt, Germany). *endo*/*exo*-5-(Bicyclohept-2-ene-5-yl)methyldichlorosilane and *endo*/*exo*-norborn-2-ene-5-yltrichlorosilane (both *endo:exo*=4:1) were purchased from ABCR (Karlsruhe, Germany). *endo*-Norborn-2-ene-5-carboxylic acid chloride [20], and the initiator $Cl_2Ru(PCy_3)_2(CHC_6H_5)$ (Cy= cyclohexyl) [21] were prepared according to literature procedures and checked for purity by means of nuclear magnetic resonance (NMR). Purchased starting materials, HPLC solvents were used without any further purification. The investigated racemic compounds were recrystallized from diethyl ether–*n*-pentane prior to use. Syntheses of norborn-2-ene-derivatized silica containing 0.25 mmol norborn-2-ene/g silica [12], *endo*/*exo*-6-*O*-(norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tris(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tetrakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, hexakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tetrakis(*endo*-6-*O*-norborn-2-ene-5-carboxyl)-β-CD as well as of **1a**, **1b**, **3a**, **3b** are described elsewhere [6,9,10]. Grafting of the monomers was carried out as described earlier [12].

2.1. 2-Ferrocenyl-5-iodobenzoic acid [6]

5-Iodoanthranilic acid (66.85 g, 269.5 mmol) was suspended in a mixture of 800 ml of water and 400 ml of concentrated hydrochloric acid. A solution of sodium nitrite (18.94 g, 283.0 mmol) in 200 ml of water was added at 0 °C. After stirring the solution for another 30 min, a solution of ferrocene (75.20 g, 404.3 mmol) dissolved in a mixture of 5 ml of acetonitrile (ACN) and 900 ml of toluene was added. After stirring overnight, sodium hyposulfite was added and the aqueous solution was extracted with diethyl ether (4×200 ml). The combined organic layers were extracted with ammonium hydroxide solution (3×100 ml). The aqueous solution was acidified with hydrochloric acid and extracted with diethyl ether (3×100 ml). The crude product was purified by addition of 30 g of silicaG60 (Fluka 60741), removal of the diethyl ether in vacuo and Soxhlet extraction of the target compound using 700 ml of hexane. Yield: 46.74 g (40%). Melting point (m.p.) 115–117 °C; IR (KBr): 3425 b, 3078 m, 2966 m, 2364 w, 1705 vs, 1580 w, 1553 m, 1497 m, 1449 m, 1383 m, 1297 s, 1277 s, 1262 s, 1246 s, 1206 m, 1156 w, 1106 s, 1088 w, 1034 w, 1001 m, 890 s, 822 vs, 805 m, 724 w, 704 m, 654 m, 598 m, 540 m, 507 s, 477 m. MS (EI, 70 e V): m/z=432 ($M^{+\cdot}$, 23%), 431 ($M^{+\cdot}$–H, 100%), 366 ($M^{+\cdot}$–H, –Cp, 67%). ^{1}H-NMR ($CDCl_3$, TMS) δ 4.08, s, 5H), 4.33 (s, 2H), 4.51 (s, 2H), 7.1–8.5 (m, 3H). ^{13}C-NMR ($CDCl_3$, TMS) δ 69.61, 70.27, 70.6, 90.7, 130.0, 130.9, 134.1, 138.6, 140.5, 143.4.

2.2. 6-Iodoferroceno[2,3a]inden-1-one

A solution of 2-ferrocenyl-5-iodobenzoic acid (5.00 g, 11,5 mmol) in 200 ml of methylene chloride was cooled to 0 °C and phosphorus pentachloride (2.65 g, 12,7 mmol) was added in portions. The mixture was refluxed for 23 h, cooled to 0 °C and aluminum trichloride (1.69 g, 12,7 mmol) was added. The solution was stirred over night and finally poured on ice–citric acid (1 *M* in water). After extraction with diethyl ether, the crude product was purified by LC on silica G60, Fluka 60741, 4×9 cm, using *n*-hexane as an eluent. Yield: 3.47 g (72.4%), IR (KBr): 3072 m, 2917 m, 1698 vs, 1590 s, 1445 s, 1410 s, 1347 m, 1310 m, 1264 s, 1237 m, 1212 s, 1158 s, 1129 s, 1106 s, 1082 s, 1052 s, 1009 s, 978 w, 940 w, 888 m, 851 s, 828 s, 812 vs, 781 s, 726 s, 702 vs, 635 m, 604 s, 579 w, 558 w, 523 s, 507 vs, 494 vs, 417 m. MS (EI, 70 e V): m/z=414 $M^{+\cdot}$ 93%, 287 $M^{+\cdot}$, 35%, 222 $M^{+\cdot}$–Cp, 11%, 206 $M^{+\cdot}$–Cp, O, 12%). ^{1}H-NMR ($CDCl_3$, TMS) δ 4.10 (s, 5H), 4.97–4.80 (m, 3H), 6.90–6.80 (m, 1H), 7.74–7.52 (m, 2H); ^{13}C-NMR ($CDCl_3$, TMS) δ 67.2, 67.3, 67.5, 67.5, 73.8, 73.8, 76.5, 76.5, 78.3, 91.7, 122.5, 122.5, 132.6, 132.7, 142.2, 142.2, 143.4, UV (CH_3CN) λ_{max} (ϵ) 243 (27 280), 280 (23 768), 409 (1487), 511 (1803).

2.3. 1-(2-Propenyl)-1-methoxyferroceno-[2,3a]indene (**4a**, **4b**)

Ferroceno[2,3*a*]inden-1-one (300 mg, 871 mmol) was dissolved in 5 ml of diethyl ether and 1.4 ml of allylmagnesiumbromide (1 *M* in diethyl ether) was added. After 10 min, iodomethane (0.2 ml) was added, the reaction mixture was stirred overnight, quenched with water and extracted with diethyl ether (3×15 ml). Crystallization from diethyl ether yielded 345 mg (96.3%) of the compound. m.p. 79–81 °C. IR (KBr): 3083 m, 2966 s, 2933 m, 2854 w, 2825 m, 1640 m, 1611 m, 1505 w, 1465 m, 1436 m, 1414 m, 1368 w, 1322 w, 1302 w, 1262 vs, 1185 m, 1015 vs, b, 926 s, 863 m, 803 vs, 760 s, 714 m, 685 w, 666 m, 644 w, 600 s, 581, 565 w, 552 m, 523 s, 469 s. MS (EI, 70 e V): m/z=344 $M^{+\cdot}$, 66%, 303 $M^{+\cdot}$–CH_2–$CH{=}CH_2$, 100%, 288 M^{+}–CH_3, CH_2–$CH{=}CH_2$ 50%. ^{1}H-NMR ($CDCl_3$, TMS) δ 2.45–2.55 (m, 1H), 2.72–2.82 (m, 1H), 3.66 (s, 3H), 3.97 (s, 5H), 4.17 (d, 1 H), 4.22 (t, 1 H), 4.39 (d, 1H), 4.70–4.86 (m, 2H), 5.25–5.45 (m, 1H), 7.05–7.25 (m, 4H). ^{13}C-NMR ($CDCl_3$, TMS) δ 42.1, 52.5, 60.0, 64.2, 71.0, 84.4, 91.2, 70.8, 96.0, 118.4, 120.7, 124.7, 126.1, 128.8 133.8, 140.2, 151.7.

2.4. 6-(3-Hydroxy-3-methylbut-1-yn-1-yl)-ferroceno[2,3a]inden-1-one (**2a**, **2b**)

6-Iodoferroceno[2,3*a*]inden-1-one (0.226 g, 0.546 mmol) was suspended in 2-methyl-3-butyne-2-ol (0.17 g, ca. 2 ml, 20 mmol) and 2 ml of triethylamine (TEA). Triphenylarsine (5 mg) and bis-(dibenzylideneacetone)-palladium (5 mg) were added and the solution was stirred for 48 h. The volatiles were removed in vacuo and the residue was purified by LC on silica G60 (Fluka 60472) using *n*-hexane as mobile phase. Yield: 118 mg (58.4%), m.p. 75 °C. IR (KBr): 3450 b,s, 3097 m, 2979 s, 2929 m, 1607 vs, 1600 s, 1574 w, 1451 vs, 1418 m, 1362 m, 1314 m, 1287 m, 1262 m, 1237 m, 1214 w, 1167 m, 1121 m, 1108 m, 1075 w, 1044 w, 1017 w, 963 m, 938 m, 893 m, 835 b,s, 785 m, 733 w, 698 w, 650 w, 612 w, 509 m, 457 m. MS (EI, 70 e V): m/z=370 $M^{+\cdot}$ 100%, 310 $M^{+\cdot}$–FeCp 84%. ^{1}H-NMR ($CDCl_3$, TMS) δ 1,55 (s, 6 H), 2,41 (s, 1H), 4.03 (s, 5H), 4.80–4.82 (m, 2H), 4.92–4.94 m, 1H), 6.98–7.45, m, 3H). ^{13}C-NMR ($CDCl_3$, TMS) δ 32.2, 66.2, 67.4, 73.1 73.4, 73.8, 74.95, 75.0, 76.5, 79.1, 86.3, 90.2, 95.3, 120.6, 126.8, 137.0, 133.0, 134.2, 141.1, 194.8.

2.5. 1,4-Dihydroxybutylferrocene (**5a**, **5b**)

This compound was synthesized via reduction of 4-ferrocenyl-4-oxobutanal by lithium triethylboranate [22]. Analytical data were identical to those reported in the literature.

3. Results and discussion

3.1. Synthesis of ligands and supports

Cyclodextrin-based selectors were used in form of *endo*/*exo*-6-*O*-(norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tris(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, tetrakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD, hexakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD and tetrakis(*endo*-6-*O*-norborn-2-ene-5-carboxyl)-β-CD (Fig. 2).

The synthesis of these compounds has been reported in detail earlier [9,10]. Briefly, β-CD was dried in refluxing toluene using a Dean Stark apparatus and reacted with *endo*/*exo*-norborn-2-ene-5-yl-methyldichlorosilane and *endo*-norborn-2-ene-5-carboxylic chloride, respectively.

Supports were synthesized by ring-opening metathesis graft polymerization. A detailed description of the grafting procedure is given elsewhere [9,11,12]. Briefly, the synthesis is accomplished by a simple surface derivatization with copolymerizable anchoring groups followed by the use of a well-defined grafting chemistry for the attachment of the corresponding selector. This approach offers access to comparably stable supports (stable within 2<pH< 10) as well as to higher β-CD loadings. In a first step, silica was reacted with norborn-2-ene-5-yltrichlorosilane. The total amount of norborn-2-ene groups attached to the support was 0.25 mmol/g. Subsequent ''endcapping'' with a mixture of chlorotrimethylsilane and dichlorodimethylsilane led to a sufficient derivatization of a major part of the surface silanol groups. In a second step, the initiator [$Cl_2Ru(=CHPh)(PCy_3)_2$ (Cy=cyclohexyl)] was

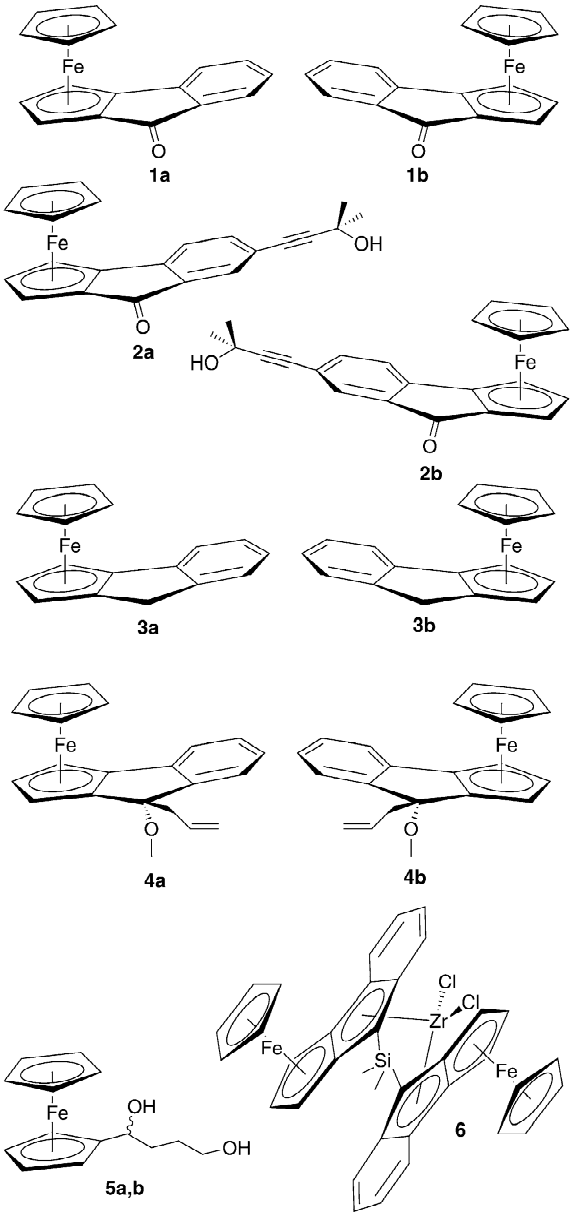


Fig. 2. Structures of β-CD-based selectors.

reacted with these surface-bound norborn-2-ene groups. Finally, β-CD-substituted, norbornene-based monomers were added to the heterogenized initiator and became grafted onto the surface. Table 1 gives an overview over the CSPs that were prepared according to this procedure.

As can be deduced therefrom, the amount of β-CD that can be attached to the surface is in the range of 11–34 μmol, corresponding to 1.2–3.9% (w/w). The fact that larger amounts of β-CD can be realized with selectors containing more than one norborn-2-ene group (11 vs. 19–34 μmol) strongly suggests the formation of cross-linked β-CD ligands at the surface. This is consistent with previous findings on the formation of such cross-linked species by solution polymerization of tris(*endo*,*exo*-6-*O*-norborn-2-ene-5-carboxyl)-β-CD [10].

3.2. Enantiomeric separations

Chiral separations of planar–chiral ferroceno[2,3*a*]inden-1-ones and ferroceno[2,3*a*]-indenes were carried out with CSPs I–V (Tables 2 and 3). Generally, enantiomeric separations were performed in the polar organic mode, using the ''magic'' mobile phase consisting of acetonitrile, methanol and triethylammonium acetate [13,14]. Interestingly, neither *rac*-ferroceno[2,3*a*]indene (**3a**, **3b**) nor the *rac*-ferroceno[2,3*a*]indene-derivatives **4a**, **4b** and **5a**, **5b** (Fig. 1) can be separated on any β-CD-based CSP. According to the literature, β-CD preferably binds to substituted ferrocenes in a way that the organometallic compound stays within the cavity [15]. In addition, even small amounts of acetonitrile (5%) were found to significantly reduce complex formation by 15% [16]. This strongly indicates a comparably low tendency for group VIIIA metallocenes to form inclusion complexes. Consequently, it is not surprising that the highly polar derivatives **5a**, **5b** show no retention at all. On the other hand, **3a**, **3b** as well as **4a**, **4b** do not possess any suitable groups that would allow a chiral discrimination of the enantiomers by the hydroxyl groups of the β-CD rim. Apparently, only **1a**, **1b** and **2a**, **2b** with the carbonyl group present can be separated. Since chiral discrimination for compounds **1a**, **1b** and **2a**, **2b** is observed with all spacers (except on CSP III for **1a**, **1b**, Tables 2 and 3) irrespective of the number of free primary hydroxyl groups and the accessibility of the bottom of the cavity, the enantiomers must selectively interact with the secondary hydroxyl groups. A representative enantiomeric separation is shown in Fig. 3, values for selectivity coefficients and resolution are summarized in Tables 2 and 3.

Table 1
Types of selectors and amounts of β-cyclodextrin (β-CD) grafted on Nucleosil-300-5-based CSPs I–V

CSP	Selector	μmol β-CD/g
I	Poly[*endo*/*exo*-6-*O*-(norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD]	11
II	Poly[tris(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD]	22
III	Poly[tetrakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD]	22
IV	Poly[hexakis(*endo*/*exo*-6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-CD]	19
V	Poly[tetrakis(*endo*-6-*O*-norborn-2-ene-5-carboxyl)-β-CD]	34

Table 2
Separation of *rac*-ferroceno[2,3*a*]inden-1-ones (**1a**, **1b**) on CSPs I, II, IV and V

	I	II	IV	V
α	1.62	1.76	1.91	1.88
R_s	0.96	1.43	2.20	2.04
$N(1)$ (1/m)	1414	868	2231	925
$N(2)$ (1/m)	1471	1452	2541	1874

Conditions: T=0 °C; flow=0.5 ml/min; ACN–MeOH–AA–TEA (99:1:0.1:0.1), UV (280 nm).

Table 3
Separation of *rac*-6-(3-hydroxy-3-methylbut-1-yne-1-yl)ferroceno[2,3*a*]inden-1-ones (**2a**, **2b**) on CSPs I–V

	I	II	III	IV	V
α	2.07	1.82	1.82	1.70	2.15
R_s	0.86	0.87	1.52	1.41	2.70
$N(1)$ (1/m)	549	428	992	1766	1171
$N(2)$ (1/m)	336	311	1023	1339	2060

Conditions: T=0 °C; flow=0.5 ml/min; ACN–MeOH–AA–TEA (99:1:0.1:0.1), UV (280 nm).

This enantioselectivity in separation mechanism was additionally confirmed by temperature dependent separations for **1a**, **1b** (see below). Since X-ray analysis data are still missing, we were not able to perform a peak assignment for either of the enantiomers of **1a**, **1b** and **2a**, **2b**.

3.3. Temperature studies

Lower temperatures generally lead to increased retention and increased resolution on β-CD-based stationary phases [17]. Fig. 4 illustrates this significant improvement in the resolution of the two enantiomers of ferroceno[2,3*a*]inden-1-one with decreasing temperature.

Compound retention factors were determined over a temperature range of 0–35 °C. Natural logarithms of the retention factors (ln k') are shown in Table 4.

The relationship between the retention factor (ln k') and temperature for a given mobile phase was

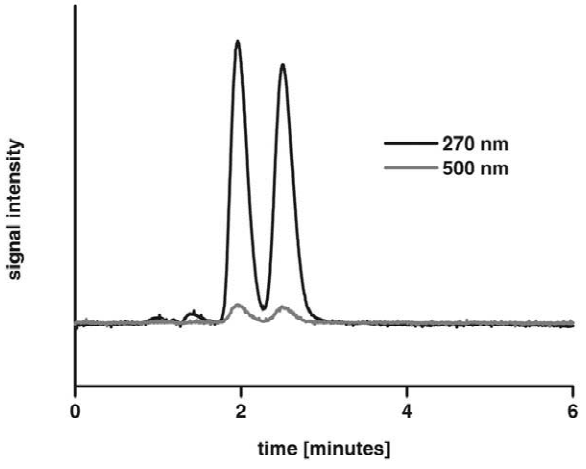


Fig. 3. Separation of *rac*-ferroceno[2,3*a*]inden-1-ones **1a**, **1b** on column III. Conditions: T=21.5 °C, flow=0.5 ml/min, ACN–MeOH–AA–TEA (90:10:0.15:0.45), UV detection.

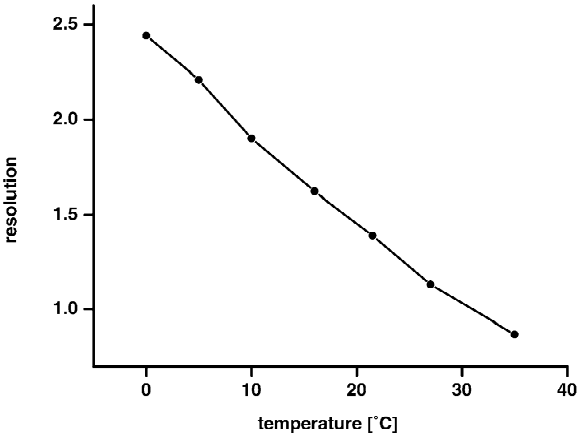


Fig. 4. Effects of temperature on resolution for **1a**, **1b** on column III. Conditions: flow=0.5 ml/min, ACN–MeOH–AA–TEA (90:10:0.15:0.45), UV (270 nm).

Table 4
Natural logarithms of the retention factors (k_i') as a function of temperature for *rac*-ferroceno[2,3*a*]inden-1-one (**1a**, **1b**) on column III

T (K)	Ln k_1'	Ln k_2'
273.5	0.158	0.790
278.5	0.090	0.690
283.5	0.074	0.621
289.5	−0.009	0.484
295	−0.090	0.376
300.5	−0.097	0.297
308.5	−0.170	0.162

derived from Van't Hoff plots. Thus, the chromatographic retention, expressed by the retention factor (k'), is related to the thermodynamic equilibrium constant (K) according to the equation $k'=K\phi$, where ϕ is the phase ratio of the column (the volume of the stationary phase divided by the volume of the mobile phase). The Gibbs free energy change for the process is expressed as $\Delta G^0=\Delta H^0-T\Delta S^0=-RT$ ln $K=-RT$ ln(k'/ϕ). Therefore, ln $k'=\Delta H^0/RT+\Delta S^0/R+$ln ϕ, where ΔG^0 is the standard Gibbs free energy of transfer of an analyte from the mobile phase to the stationary phase, ΔH^0 is the associated change in enthalpy, ΔS^0 is the associated change in entropy, R is the gas constant, and T is the absolute temperature. ΔH^0 and ΔS^0 can be derived from the slope and the intercept, respectively, and ln k' is generally a linear function of $1/T$ if only one separation mechanism is active. For the two enantiomers **1a** and **1b** (Fig. 1), the plots of ln k' versus $1/T$ can be fitted by straight lines whose correlation coefficients [R^2] are 0.998 and 0.978 (Fig. 5a).

The linearity of the plots in Fig. 5a suggests that at least in the temperature range investigated the retention process is based on only one mechanism. Analyses of the slopes of the plots yielded values for ΔH^0 of −7.3 and −12.7 kJ/mol, respectively. These are similar to those generally reported for the conventional reversed-phase mechanism (typically around −12 kJ/mol) [18,19]. Additional information is obtained from a plot of R ln α versus $1/T$ (Fig. 5b). $\Delta(\Delta H)$ and $\Delta(\Delta S)$, the differences in the dissolution enthalpy and entropy between the two enantiomers, can be calculated from the slope and intercept, respectively [23]. The corresponding values that can be derived from the linear plot ($R^2=0.992$) for

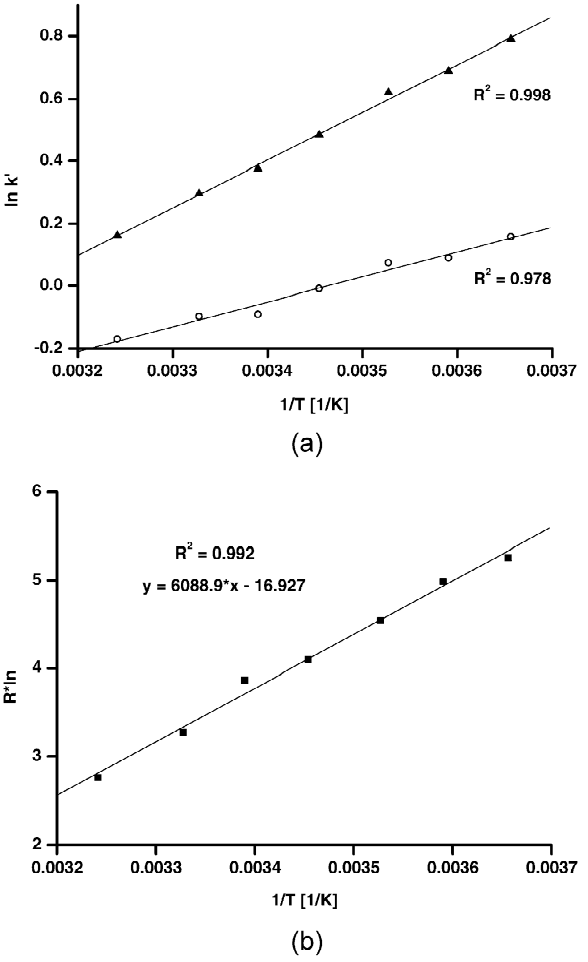


Fig. 5. (a) Plots of ln k' versus $1/T$ for **1a**, **1b** on column III. Conditions: flow=0.5 ml/min, ACN–MeOH–AA–TEA (90:10:0.5:0.45), UV (270 nm). (b) Plot of R ln α versus $1/T$ for **1a**, **1b** on column III. Conditions as in (a).

$\Delta(\Delta H)$ and $\Delta(\Delta S)$ are −6.1 kJ/mol and −16.9 J/mol K, respectively.

4. Summary

Planar chiral ferroceno[2,3*a*]inden-1-ones have successfully been separated on β-CD-based silica supports. Using the polar organic mode, the presence of the carbonyl moiety appears to be essential in order to accomplish enantiomeric separation. Thus, neither the corresponding ferroceno[2,3*a*]indenes,

alkoxyferroceno[2,3*a*]indenes nor ferrocenylalcohols could be separated.

Acknowledgements

Financial support provided by the FWF Vienna, project number Y-158 is gratefully acknowledged.

References

[1] T. Hayashi, in: A. Togni, T. Hayashi (Eds.), Ferrocenes. Homogeneous Catalysis, Organic Chemistry, Materials Science, VCH, Weinheim, 1994.
[2] C. Köllner, B. Pugin, A. Togni, J. Am. Chem. Soc. 120 (1998) 10274.
[3] A. Schnyder, L. Hintermann, A. Togni, Angew. Chem. Int. Ed. 34 (1995) 931.
[4] A. Togni, Angew. Chem. Int. Ed. 35 (1996) 1475.
[5] F. Spindler, H.-U. Blaser, Adv. Synth. Catal. 341 (2001) 61.
[6] H. Schottenberger, M. Buchmeiser, O. Elsner, E. Ernst, J. Reussner, W. Neissl, H. Angleitner, US Pat. US 5,521,265 EP 0673 946 A2, DE 4417 542 A1, AT 401 520 B.
[7] Y. Okamoto, E. Yashima, Angew. Chem. Int. Ed. 37 (1998) 1020.
[8] W. Lindner, Chromatographia 24 (1987) 97.
[9] B. Mayr, F. Sinner, M.R. Buchmeiser, J. Chromatogr. A 907 (2001) 47.
[10] K. Eder, F. Sinner, M. Mupa, C.G. Huber, M.R. Buchmeiser, Electrophoresis 22 (2001) 109.
[11] B. Mayr, M.R. Buchmeiser, J. Chromatogr. A 907 (2001) 73.
[12] M.R. Buchmeiser, F. Sinner, M. Mupa, K. Wurst, Macromolecules 33 (2000) 32.
[13] D.W. Armstrong, S. Chen, C. Chang, S. Chang, J. Liq. Chromatogr. Rel. Technol. 15 (3) (1992) 545.
[14] S.C. Chang, G.L. Reid III, S. Chen, C.D. Chang, D.W. Armstrong, Trends Anal. Chem. 12 (1993) 144.
[15] J. Liu, R. Castro, K.A. Abboud, A.E. Kaifer, J. Org. Chem. 65 (2000) 6973.
[16] D. Osella, A. Carretta, C. Nervi, M. Ravera, R. Gobetto, Organometallics 19 (2000) 2791.
[17] A. Péter, G. Török, F. Fülöp, J. Chromatogr. Sci. 36 (1998) 311.
[18] L.A. Cole, J.G. Dorsey, Anal. Chem. 64 (1992) 1317.
[19] L.A. Cole, J.G. Dorsey, K.A. Dill, Anal. Chem. 64 (1992) 1324.
[20] F. Sinner, M.R. Buchmeiser, R. Tessadri, M. Mupa, K. Wurst, G.K. Bonn, J. Am. Chem. Soc. 120 (1998) 2790.
[21] P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.
[22] C.H. Jun, J.B. Kang, J.Y. Kim, Tetrahedron Lett. 9 (1978) 839.
[23] N. Morin, Y.C. Guillaume, J.-C. Rouland, Chromatographia 48 (1998) 388.