e.g., electron-vibrational interaction.[9] Moreover, since the RAHB containing systems in solution are characterized with a double well PES with a small barrier,[5] the packing density may as well influence the PES form in the crystal.

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Separation of racemic *closo*-3,3-($\eta^{3,2}$-norbornadienyl)rhodacarboranes into enantiomers by HPLC on chiral stationary phases

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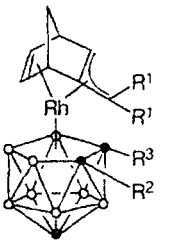
Racemic *closo*-rhodacarboranes, *viz.*, *closo*-3,3-($\eta^{3,2}$-C_7H_7-2-CR^1_2)-1-R^2-2-R^3-3,1,2-$RhC_2B_9H_9$ ($R^1 = R^2 = R^3 = H$; $R^1 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = Me$) and *closo*-2,2-($\eta^{3,2}$-C_7H_7-2-CH_2)-2,1,7-$RhC_2B_9H_{11}$, were successfully separated into enantiomers by high-performance liquid chromatography (HPLC).

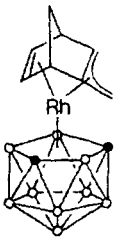
Key words: *closo*-rhodacarboranes, high-performance liquid chromatography, enantiomers, chiroptical properties.

High-performance liquid chromatography (HPLC) on chiral sorbents is one of the most convenient methods for the analysis of enantiomers and practical preparation of optically active π-complexes. This method has opened up new opportunities of obtaining high-purity enantiomers even from racemates that have no suitable functional groups for the synthesis of diastereomers and their subsequent separation by classical crystallization methods.[1,2] Only recently, HPLC has become the object of extensive use for the preparation of chiral metallacarboranes, which, however, are mostly sandwich bis(dicarbollyl)[3] and π-cyclopentadienyl-π-dicarbollyl[3,4] complexes with functional groups in the carborane ligand.

Using HPLC on chiral phases, we could separate for the first time a series of semisandwich *closo*-rhodacarboranes (*closo*-3,3-($\eta^{3,2}$-C_7H_7-2-CR^1_2)-1-R^2-2-R^3-3,1,2-$RhC_2B_9H_9$ (**1a—c**) and *closo*-2,2-($\eta^{3,2}$-C_7H_7-2-CH_2)-2,1,7-$RhC_2B_9H_{11}$ (**2**)) into enantiomers.



1a—c



2

	a	b	c
R^1	H	H	Me
R^2	H	Me	Me
R^3	H	Me	Me

Racemic complexes **1a** and **2**, which are known to be highly efficient catalysts for the diastereoselective hydrogenation of metacycline,[5,6] could be separated on

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a micropreparative scale. The amounts of the isomers obtained were sufficient to study their chiroptical and then catalytic properties.

Chromatographic separation of complexes **1** and **2** into enantiomers was performed on Astec (USA) columns (250 × 4.6 mm) packed with chiral sorbents based on β- and γ-cyclodextrin (CD) derivatives; MeOH was the eluent. Retention factors for the enantiomers (k_1' and k_2'), selectivity of separation ($\alpha = k_2'/k_1'$), racemates, and chiral sorbents are given below.

Racemate	Chiral sorbent	k_1'	k_2'	α
1a	Acetyl-β-CD	0.25	0.36	1.4
	2-Hydroxypropyl-β-CD	1.33	1.64	1.2
	(*R*)-*N*-[1-(1-Naphthyl)ethyl]-carbamoyl-β-CD	1.30	2.36	1.8
1b	γ-CD	0.86	0.93	1.1
1c	γ-CD	0.49	0.52	1.1
2	2-Hydroxypropyl-β-CD	1.00	1.20	1.2

It is noteworthy that introduction of methyl substituents both into the $\eta^{3,2}$-dienyl and the η^5-dicarbollyl ligands of complex **1a** has apparently hindered the formation of inclusion compounds with β-CD and its derivatives. That is why complexes **1b,c** were resolved analytically only on a sorbent containing γ-CD, where the enantiomers are retained much more strongly. Nonsubstituted complexes **1a** and **2** react rather actively with β-CD and its derivatives, and a high degree of enantioselectivity was attained. The optical activity of the enantiomeric complexes obtained from **1a** and **2** was determined. Enantiomers (−)-**1a** and (+)-**1a** were characterized by circular dichroism spectra (Fig. 1). These spectra were obtained on a JASCO G-720 spectropolarimeter. Enantiomers, their concentrations (C) in CH_2Cl_2, and $[\alpha]^{20}_{476}$ are given below.

Enantiomer	$C \cdot 10^4$/g mL^{-1}	$[\alpha]^{20}_{476}$/deg
(−)-**1a**	6.0	−46.33
(+)-**1a**	5.3	+46.42
(−)-**2**	2.0	−17.07
(+)-**2**	2.8	+15.86

Racemic complexes **1a,b** and **2** were synthesized as described previously[7]; **1c** was obtained in 71% yield by the reaction of $[(\eta^4\text{-}C_7H_7\text{-}2\text{-}COHMe_2)RhCl]_2$ with $[nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-K^+$ in $EtOH/C_6H_6$. ^1H and ^{13}C NMR spectra were recorded on a Brucker AMX-400 spectrometer (400.13 and 100.61 MHz, respectively) with Me_4Si as an internal standard. Compound **1c**, ^1H NMR (CD_2Cl_2), δ: 4.61 (m, 1 H, H(5)); 4.04 (m, 1 H, H(3)); 3.99 (pseudotriplet, 1 H, H(6)); 3.74 (m, 1 H, H(4)); 3.60 (m, 1 H, H(1)); 2.22 (s, 3 H, Me); 2.14 (s, 3 H, Me); 1.85 (d.t, 1 H, H(7α), $^2J_{AB}$ = 9.8 Hz, ^3J = 1.6 Hz); 1.72 (d.t, 1 H, H(7β), $^2J_{AB}$ = 9.8 Hz, ^3J = 1.6 Hz); 1.68 (s, 3 H, Me_{carb}); 1.60 (s, 3 H, Me_{carb}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ, $J_{^{13}C-^{103}Rh}$: 90.33 (d, C(2), J = 3.6 Hz); 75.45 (d, C(5), J = 5.0 Hz); 71.98 (m, C_{carb}); 70.70 (d, C(6), J = 4.5 Hz); 64.19 (m, C_{carb}); 56.44 (d, C(7), J = 2.4 Hz); 45.01 (d, C(4), J = 1.7 Hz); 42.83 (s, C(1)); 34.77 (d, C(3), J = 10.3 Hz); 32.68 (br.s, C(8)); 27.93 (s, Me_{carb}); 27.70 (s, Me_{carb}); 26.05 (s, Me); 25.49 (s, Me).

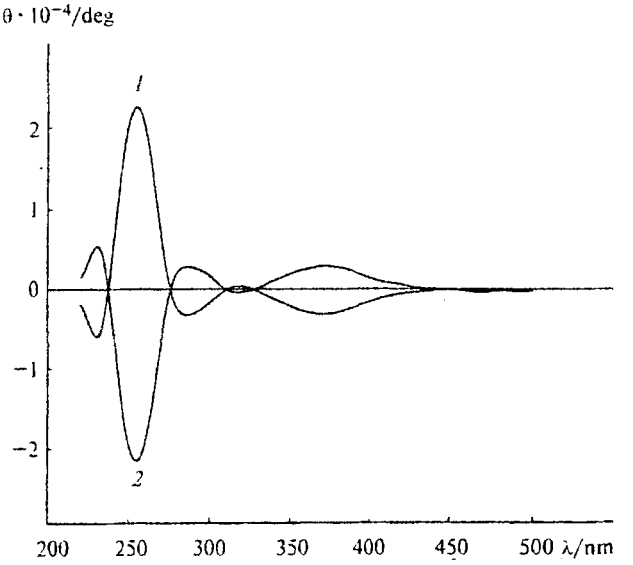

Fig. 1. Circular dichroism spectra of enantiomeric complexes (*1*) (−)-**1a** and (*2*) (+)-**1a** in methanol.

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