Synthesis and configurational assignment of diastereomers of *closo*-3,3-[$\eta^{2,3}$-(2-methylenebicyclo[2.2.1]hepta-2,5-dien-2-yl)]-1-benzyl-3,1,2-dicarbollylrhodium complexes

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The previously synthesized mixture of diastereomeric complexes *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1-($PhCH_2$)-3,1,2-$RhC_2B_9H_{10}$ was separated by TLC on silica gel into individual diastereomers, whose stereochemistry and relative configurations were determined by X-ray diffraction analysis.

Key words: *closo*-rhodacarboranes, configurational assignment, X-ray diffraction analysis.

closo-Rhodacarboranes with the 2-methylenenorbornadienyl ligand[1] are efficient catalysts of the diastereoselective hydrogenation of metacycline to form the known antibiotic doxycycline.[2,3] From this viewpoint, synthesis of novel and especially stereochemically individual metallacarboranes of a similar type is significant.

In this work, we report on the separation of a mixture of diastereomeric complexes *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1-($PhCH_2$)-3,1,2-$RhC_2B_9H_{10}$ (**1**) into individual isomers (**1a** and **1b**). Relative configurations were objectively established for each of these isomers by the X-ray diffraction method. The previously obtained[4] mixture of diastereomers **1** was quantitatively separated into isomers **1a** (R_f = 0.71, m.p.(dec.) 215 °C) and **1b** (R_f = 0.66, m.p.(dec.) 220 °C) by TLC on silica gel. Diastereomeric purity of the complexes was monitored by ^{1}H NMR (CD_2Cl_2), δ: **1a**, 7.37, 7.16 (m, 5 H, Ph), 4.68 (q*, 1 H, H(5)), 4.39 (t*, 1 H, H(3)), 4.22 (s, 1 H, H_{syn}(8)), 4.01 (br.s, 1 H, CH of carborane), 3.80 (t*, 1 H, H(6)), 3.65 (m, 1 H, H(4)), 3.55, 3.38 (d, 2 H, CH_2Ph, J_{AB} = 14.5 Hz), 3.26 (m, 1 H, H(1)), 3.20 (s, 1 H, H_{anti}(8)), 1.89 (dq, α(β)-H(7), J_{AB} = 10.2, J_q = 1.4 Hz), 1.74 (dt, β(α)-H(7), J_{AB} = 10.2, J_t = 1.6 Hz); **1b**, 7.32, 7.14 (m, 5 H, Ph), 5.33 (s, 1 H, H_{syn}(8)), 4.97 (t*, 1 H, H(5)), 4.31 (t*, 1 H, H(3)), 3.88 (s, 1 H, H_{anti}(8)), 3.86 (t*, 1 H, H(6)), 3.79 (m, 1 H, H(4)), 3.63 (br.s, 1 H, CH of carborane), 3.46 (m, 1 H, H(1)), 3.44, 3.17 (d, 2 H, CH_2Ph, J_{AB} = 14 Hz), 1.88 (dm, 1 H, α(β)-H(7), J_{AB} = 10.2 Hz), 1.87 (dt, 1 H, β(α)-H(7), J_{AB} = 10.2, J_t = 1.7 Hz). The spectra of the diastereomeric complexes are characterized by the difference in shielding of the α,β-H(7) protons of the AB system: $\Delta\delta_{AB}$ values for **1a** and **1b** (CD_2Cl_2, 22 °C, 400.13 Hz) are 0.15 and 0.01, respectively.

*Triplet- and quadruplet-like signals are marked with an asterisk (*).

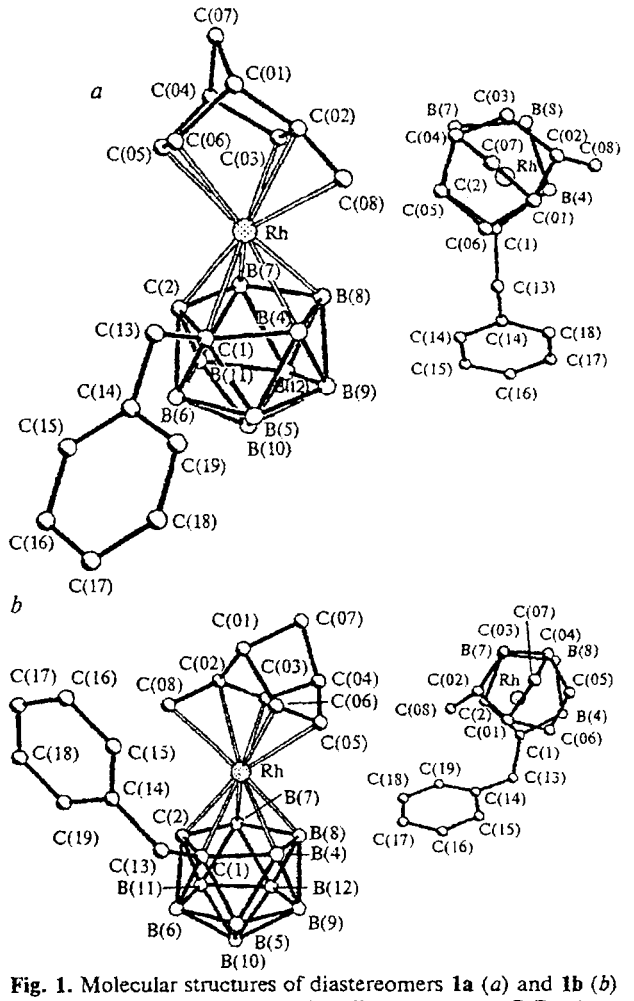

Fig. 1. Molecular structures of diastereomers **1a** (*a*) and **1b** (*b*) and projections of the hydrocarbon ligand onto the C_2B_3 plane (boron atoms of the lower belt of the π-dicarbollyl ligand are not shown).

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Both diastereomers (Fig. 1) are crystallized from the n-C_6H_{14}—CH_2Cl_2 mixture as racemates in the centrosymmetric space groups *Pbca* (**1a**) and $P2_1/c$ (**1b**). The (*RS*)- and (*SS*)-configurations relative to the chiral C(01) and C(1) centers should be assigned to those enantiomers of diastereomeric complexes **1a** and **1b**, respectively, which are presented in Fig. 1, and thus, it can be asserted that crystals of **1a** and **1b** are (*RS/SR*)- and (*SS/RR*)-diastereomers.

The different orientations of the norbornadienyl ligands relative to the substituent in the pentagonal C_2B_3 plane of the carborane ligand (see projections in Fig. 1 to the right from the structures) are an important stereochemical feature of diastereomers **1a** and **1b**, which could be explained by the steric effect of the substituent in monosubstituted complexes of this type. However, the orientation of the norbornadiene ligand, which is similar to that in **1a**, has been previously observed in three independent molecules of the nonsubstituted *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-3,1,2-$RhC_2B_9H_{11}$ complex[3] as well as in the crystal of *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$,[1] although in the latter case, this orientation of the dienyl ligand in the complex results in a short nonbonded contact (3.074 Å) between the exocyclic carbon C(08) atom and the carbon atom of the nearest methyl substituent in the carborane ligand. Therefore, not only steric, but also electronic factors should be taken into account to explain the different orientations of the norbornadiene ligand in the complexes studied.

Experimental

^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer with a working frequency of 400.13 MHz using CD_2Cl_2 as the solvent and TMS as the internal standard. TLC was carried out on silica gel (Silpearl) using the n-C_6H_{14}—$CHCl_3$ (1 : 2) mixture as the eluent.

Crystals of **1a** are orthorhombic; at −120 °C a = 16.131(3), b = 12.336(4), c = 19.561(4) Å, V = 3892.5(5) Å^3, d_{calc} = 1.470 g cm^{-3}, Z = 8, space group *Pbca*. Crystals of **1b** are monoclinic; at −120 °C a = 11.411(5), b = 13.061(5), c = 13.070(6) Å, β = 96.33(4)°, V = 1936.0(9) Å^3, d_{calc} = 1.477 g cm^3, Z = 4, space group $P2_1/c$. Parameters of unit cells and intensities of 3092 independent reflections with $F^2 \geq 4\sigma$ for **1a** and 2057 independent reflections with $F^2 \geq 3\sigma$ for **1b** were measured on a Syntex $P2_1$ four-circle automated diffractometer (−120 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scan mode, θ ≤ 30°).

Both structures were solved by the direct method and refined by the full-matrix least-squares method first in the isotropic and then anisotropic approximations. All hydrogen atoms in the both structures were localized in the difference synthesis and included into the refinement with the fixed coordinates and isotropic temperature factors. The resulting R-factors were 0.041 and 0.069 (R_W = 0.042 and 0.074) for **1a** and **1b**, respectively. All calculations were performed on an Eclips S/200 computer by the INEXTL program.[5]

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