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Resolution of the [6,6′-μ-$(CH_3)_2$P-(1,7-$(C_2B_9H_{10})_2$)-2-Co] bridged cobaltacarborane to enantiomers pure by chiral HPLC, circular dichroism spectra and absolute configurations by X-ray diffraction

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Abstract

Racemic [6,6′-μ-$(CH_3)_2$P-(1,7-$(C_2B_9H_{10})_2$)-2-Co] zwitterion **1R** was resolved into enantiomers **1A** and **1B** by chiral HPLC, and, for the first time for a chiral metallacarborane, absolute configurations of both enantiomers were determined by X-ray diffraction. HPLC results, circular dichroism spectra and crystallographic data [orthorhombic, space group $P2_12_12$, Z=8; **1A**: a=11.5180(5) Å, b=12.4741(6) Å, c=13.8335(8) Å, V=1987.6(2) Å^3, **1B**: a=11.5177(3) Å, b=12.4700 Å, c=13.8326(6) Å, V=1986.7(1) Å^3] are presented. Nomenclature and correlation of the CD curves with those reported earlier for closely related analogs, are discussed, along with general implications for chiral HPLC resolutions on a β-cyclodextrin column.

On treatment of the $[(1,7\text{-}C_2B_9H_{11})_2\text{-}2\text{-}Co]^-$ ion with various reagents under electrophilic conditions, a variety of B–E–B bridged species results where E (bridge)=O, S, N, P.[1–4] From these reactions the corresponding racemic forms were exclusively obtained; the presence of the *meso*-form was not observed in the resulting products. These aspects have already been discussed in previous communications summarizing synthetic results.[1–3] The general formula of all these compounds is [6,6′-μ-R_nE-(1,7-$C_2B_9H_{10})_2$-2-Co]. Most of the racemic species were resolved into enantiomers using high performance liquid chromatography on Chiral Stationary Phases (CSPs) and the respective circular dichroism (CD) spectra were measured.[5,6] HPLC results for sulfur and nitrogen bridged analogues were summarized in a preliminary review.[7] X-Ray structures have been reported for two members of this family: the anion with a sulphur bridge[4] and for the $Me_2P<$ bridged racemic compound.[3]

Here we report a semi-preparative enantioseparation of the last member, the [6,6′-μ-$(CH_3)_2$P-(1,7-$C_2B_9H_{10})_2$-2-Co] racemic zwitterion **1R** (Fig. 1) into respective enantiomers **1A** and **1B**. Their CD

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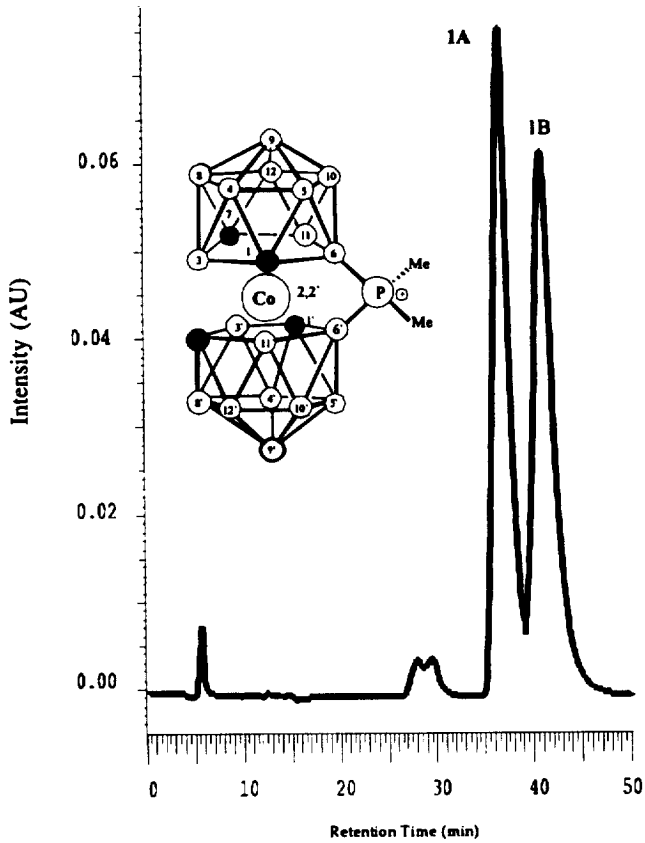

Fig. 1. Analytical HPLC separation of the enantiomers of the zwitterionic [6,6′-μ-$(CH_3)_2$P-(1,7-$C_2B_9H_{10})_2$-2-Co] **1R** on a native β-cyclodextrin column. For chromatographic conditions see the Experimental

spectra, and the first successful determination of the absolute configurations of both enantiomers by X-ray diffraction in a carborane and metallaborane series are presented. The implications of these new results on understanding of the separation mechanism on native β-cyclodextrin CSPs and the correlation of the CD spectra within the whole family is discussed, along with nomenclature problems.

1. Experimental

The chromatographically pure **1R** (2.0 g) was prepared as published recently[3] and checked for the parameters described there. 10 mg of **1R** was used for this study.

*1.1. HPLC resolution of **1R** to the enantiomers **1A** and **1B***

1.1.1. Equipment

Analytical system: Merck–Hitachi 6200 intelligent pump, D-6000 interface, Rheodyne 7125 injection valve with 20 μl sample loop, L 7450 diode array detector with 7000 Manager software 2.1. Preparative system: micropump LCP 3001, Rheodyne 7010 injection valve with 100 μl sample loop, UV–vis variable wavelength detector LCD 2040, a laboratory-made splitting 6-way valve, TZ 4200 line recorder (ECOM Prague).

1.1.2. Chemicals, sample preparation and chromatographic conditions

Deionized water was used for the preparation of aqueous–organic mobile phases. All other chemicals were of analytical grade (Lachema Brno, Czech Republic). Methanol was distilled before use. Eluents were filtered through a 0.45 μm filter and shortly degassed under vacuum. Samples were prepared just before injection as methanolic solutions of concentrations 2.0 mg/ml. All samples were filtered through a 0.45 μm Teflon micro filter (Tessek Ltd, Czech Republic).

Chromatographic conditions: a stainless steel HPLC column was slurry-packed with native β-cyclodextrin CSP with high cyclodextrin loading (carbon content 9%) (250×8 mm ID). The column was used for both analytical and preparative separation. The void volume of the β-cyclodextrin column was determined according to the literature method[8]; mobile phase: 80% aqueous methanol, flow rate 0.8 ml/min, injection: 5 μl for an analytical injection, 100 μl for a preparative injection. The eluent from the ascending part of the first peak and from the descending part of the second peak was collected. Compounds of type **1** were detected at fixed wavelengths 270 and 285 and 295 nm in the analytical run, sensitivity range 0–0.2 AUFS and at 280 nm during the preparative separations, sensitivity 1.28 AUFS. The following optimum chromatographic parameters were obtained. Analytical separation: capacity factors, k_{1A}'=5.38, k_{1B}'=6.11; selectivity=1.14; resolution R_s=1.32. Preparative separation: k_{1A}'=5.02, k_{1B}'=5.71; selectivity=1.14; resolution R_s=1.10.

1.1.3. Preparation of monocrystals of 1A and 1B

Separated fractions containing **1A** and **1B**, respectively, from 40 runs were combined, the solvents were removed under vacuum and the crystalline residues of **1A** and **1B** (1.5 mg) were dissolved in 0.25 ml of benzene. The filtered solutions were transferred into NMR tubes with 4.5 mm i.d. and carefully covered with 1 ml of hexane. After several weeks at ambient temperature, deep red crystals appeared in each tube. The mother liquors were decanted, the crystals were rinsed with hexane and dried under vacuum at 25°C. A randomly selected crystal of each enantiomer was examined by X-ray diffraction. Crystals after measurements were re-dissolved in methanol and their optical purity was rechecked by HPLC. No change in enantiomeric excess occurred during the above procedures.

1.1.4. Circular dichroism spectra

Quantities of the samples (0.25 mg) were dissolved in methanol (1 ml) prior to measurements (concentration 6.51×10^{-4} mol/l). The CD spectra were recorded on Auto Dichrographe Mark V equipment, (Jobin Yvon, France). The instrument is driven by a microcomputer (Silex, France) loaded with IOCB AS (R software). The measurements were performed in quartz cells with an optical path length of 0.98 mm. The spectra are computer averages over three instrument scans and the intensities are presented in terms of $\Delta\varepsilon$ values.

1.1.5. X-Ray diffraction

The crystals of **1A** and **1B** were mounted on glass fibres with epoxy cement and measured on four circles diffractometer CAD4-MACHIII with graphite-monochromated MoK_α radiation. The crystallographic details are summarized in Table 1. The structure of **1B** was solved by the heavy atom method (SHELXS86[9]) and refined by a full matrix least squares procedure based on F^2 (SHELXL93[10]). For the solution of the **1A** structure the coordinates of **1B** were used as the starting model. Hydrogen atoms were localized on a difference Fourier map and refined isotropically. The final difference map had no peaks of chemical significance. Scattering factors were those implemented in the SHELX programs. The absolute structure for both crystals was determined using chirality parameter x.[11] Numerical absorption correction

Table 1
Crystallographic data for **1A** and **1B**

	1A	**1B**
	(a) Crystal Parameters	
formula	$C_6H_{26}B_{18}CoP$	$C_6H_{26}B_{18}CoP$
	382.75	382.75
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12$ (No.18)	$P2_12_12$ (No.18)
a, Å	11.5180(5)	11.5177(3)
b, Å	12.4741(6)	12.4700(4)
c, Å	13.8335(8)	13.8326(6)
V, Å^3	1987.6(2)	1986.7(1)
Z	8	8
d(calcd), g/cm^3	1.279	1.280
μ(Mo K_α), mm^{-1}	0.931	0.931
T(min),T(max)	0.544;	0.596
temperature, K	293(2)	293(2)
crystal size, mm	0.46x0.78x0.8	0.75x0.69x0.67
	deep red	deep red
	(b) Data Collection	
data collection method	ω –2 scans	ω–2 scans
scan limits (Θ), (°)	0≤ 30	0 ≤30
data collected: *h*	± 16	-13,16
k	± 17	-15,17
l	±19	± 19
reflections collected	6514	4428
reflections unique (R_{int})	5793(0.0082)	4206 (0.0093)
reflections observed ($\|F_o\| \geq 4\sigma(\|F_o\|)$)	4678	3472
	(c) Refinement	
R(F), %[a]	3.04	2.05
R(wF), %[b]	8.94	7.53
GOF[d]	1.072	1.069
chirality parameter x	-0.00(2)	-0.03(2)

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; [b] $wR2 = [\sum[(w(F_o^2 - F_c^2)^2]/[\sum w(F_o)^2]]^{0.5}$; $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$;

$P = [max(F_o^2) + 2F_c^2]/3$; $w_1(w_2) = 0.00566(0.1377)$; for **1A**; 0.0418(0.1718) for **1B**; [d] GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(N_n - N_v)]^{0.5}$

for the crystal of **1B** was made during data reduction, using program JANA96. For the crystal of **1A**, the absorption was neglected (μR=0.65).

2. Results and discussion

The recent introduction of HPLC techniques for enantiomeric separation in the field of chiral carborane and metallaborane derivatives has led to accelerated development in this area over the past five years. The use of native,[5–7,12–14] or functionalized[7,14] β-cyclodextrin CSPs allowed the enantioseparation even on a semi-preparative scale of a broad range of such chiral species into enantiomers. The preparative separation of enantiomers **1A** and **1B** was carried out on native β-cyclodextrin CSP in a procedure similar to that described for 13 closely related bridged chiral cobaltacarborane derivatives.[6,7] The chromatographic conditions including mobile phase composition (75–85% aqueous MeOH), flow rate (1.6–0.8 ml/min), detection (270–340 nm) and column loading were optimized in a similar manner as for the previously reported series of cobaltacarboranes,[6] for details see the Experimental. The efficiency of this separation carried out under optimum chromatographic conditions is shown by the chromatogram

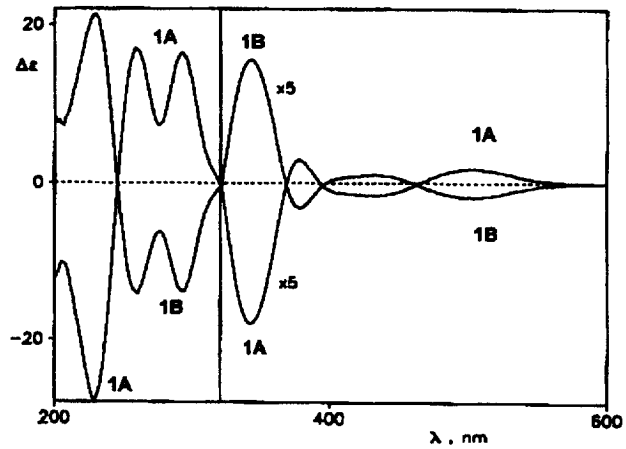

Fig. 2. Circular dichroism spectra of the first eluting **1A** and the second eluting **1B** enantiomers

in Fig. 1. The enantiomeric excess of both enantiomers was higher than 98% and 90% for **1A** and **1B** respectively, as assessed by analytical HPLC. The high purity of enantiomers is also apparent from the almost perfect complementary CD curves in Fig. 2. Again, the faster moving enantiomer shows the same general pattern of CD peaks as do all 13 faster analogs reported earlier,[6,7] thus supporting the presumption that the first eluted enantiomers possess the same absolute configuration. Consequently, the same subtle effect in the orientation of molecules in the β-cyclodextrin cavity is apparently always responsible for a less tight intercalation of these enantiomers.

The series of species of type **1** might be an ideal model for the study of the intercalation separation mechanism of enantiomers on β-cyclodextrin chiral HPLC supports; they have the same shape and essentially the same dimensions, there are no lone electron pairs on the metallacarborane frameworks, and there is the same asymmetry in the charge distribution around the circumference of both pentagonal ligand planes. The presence of the bridging atom apparently plays a significant role in the chiral resolution of compounds of type **1**, but the nature of the bridging atom has only minor influence on the chromatographic resolution and selectivity. The bridge fixes both deltahedral ligands for prochiral arrangement, giving the molecule a high rigidity. Neither the number nor the size and polarity of the bridge pendant groups prevent enantiodiscrimination, but, to some extent, influence the selectivity and resolution.[6] Most probably, only steric requirements of these groups account for the enantioselectivity. The mutual inclination of both icosahedral ligands for different bridging atoms, decreasing in the series O≥N>S>P as discussed elsewhere[3] does not seem to affect the resolution.

In this particular case, the diameter of the β-cyclodextrin cavity (7.80 Å) is equal to its depth[15] and is too small to allow penetration of the whole species of type **1** into the cavity. Apparently, only one of the icosahedra might fit into the cavity, leaving the bridging group and the second carborane moiety outside. This view is supported by the minor role of mutual inclination of both deltahedral ligands in the resolution of enantiomers.

The arrangement of CH vertices at the circumference of the pentagonal ligand plane within the deltahedral ligand seems to be the most decisive factor for the enantiodiscrimination of **1A** and **1B** on the β-cyclodextrin support. These vertices bear a partial positive charge that might exert Coulombic attraction to the electron rich oxygen atoms residing on the rim of the β-cyclodextrin cavity.

The absolute configuration of both enantiomers **1A** (Fig. 3) and **1B** (Fig. 4) were established and will be discussed below. Now that the absolute configuration of **1A** and **1B** is known (for their mirror image see Fig. 5), it is clear that the arrangement of skeletal C–H vertices in **1A** is less suitable for accommodation

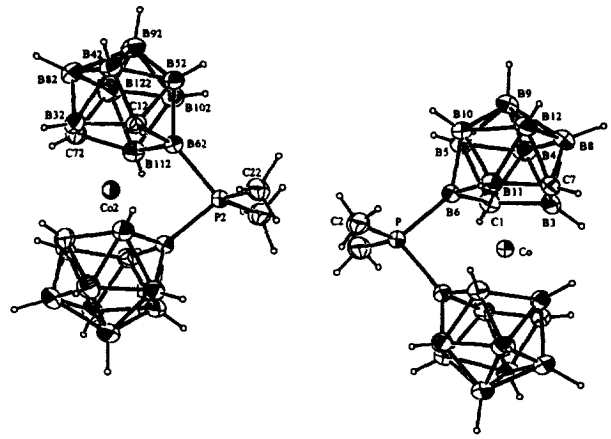

Fig. 3. An ORTEP presentation of the asymmetric unit of the enantiomer **1A**

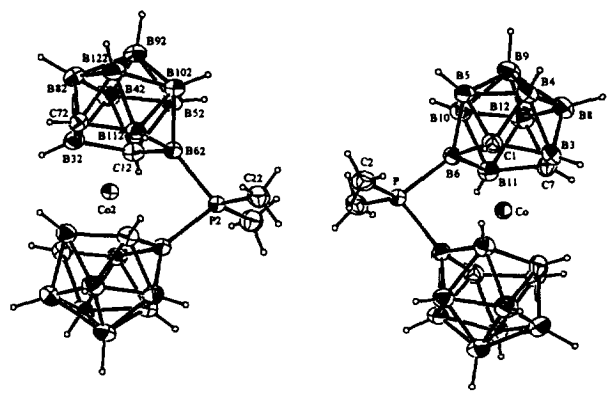

Fig. 4. An ORTEP presentation of the asymmetric unit of the enantiomer **1B**

in the β-cyclodextrin matrix than is that in the **1B** enantiomer, and therefore **1A** (and its 13 analogs, reported earlier[8,9]) is eluted first.

2.1. *X-Ray crystal structure studies*

As expected, the general features of molecules of **1A** and **1B** (Figs 3 and 4, Tables 1–4) are close to those determined from racemic crystal[3] **1R**. However, these crystals resemble the racemic one also in cell dimensions [a=11.478(2) Å, b=12.438(6) Å, c=13.771(4) Å, 90, 90, 90, V=1965.9 Å^3]. The most remarkable differences are in length of the c axis, which is 0.062 shorter in the racemic crystal, and in the volume of the unit cell, which is in **1R** about 20.8 Å^3 smaller than in **1A** and **1B**. Also, the molecular packings are similar to each other since the Co and P atoms are in special positions on the two-fold axis in **1A** and **1B**. Moreover, the two symmetrically independent molecules in space group $P2_12_12$ of **1A** and **1B** fulfil the condition of mutual centrosymmetricity, except for the C1, C7 and the C12, C72 carbon atom positions of the two carborane cages. Consequently, the diffractions that shall be systematically absent in the Pnca space group of the racemic crystal are very weak in **1A** and **1B**. The strongest of them were repeatedly measured with a different ψ angle value to eliminate the possibility of the Renninger effect. To enhance the reliability of the absolute structure determination, the complete sets of the Friedel's

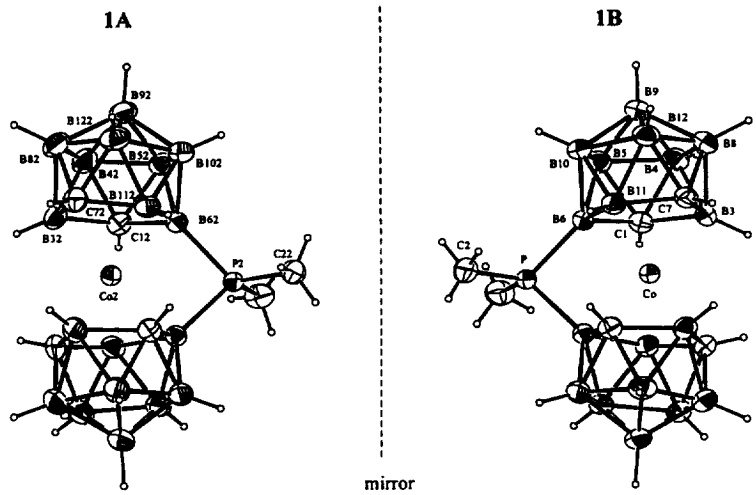

Fig. 5. Mirror image of molecules of both enantiomers **1A** and **1B**

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$ Å) for **1A**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Co	5000	0	-6275(1)	23(1)
P	5000	0	-4171(1)	24(1)
C(2)	6275(2)	115(2)	-3423(2)	39(1)
C(1)	5986(2)	1331(2)	-5870(2)	29(1)
B(3)	5598(2)	1284(2)	-7064(2)	34(1)
B(4)	5931(2)	2519(2)	-6451(2)	37(1)
B(5)	5449(2)	2396(2)	-5239(2)	32(1)
B(6)	4850(2)	1084(2)	-5152(2)	24(1)
C(7)	4128(2)	1217(2)	-7057(2)	34(1)
B(8)	4710(2)	2454(2)	-7223(2)	41(1)
B(9)	4594(2)	3115(2)	-6084(2)	39(1)
B(10)	3901(2)	2194(2)	-5263(2)	33(1)
B(11)	3598(2)	1003(2)	-5939(2)	30(1)
B(12)	3470(2)	2275(2)	-6494(2)	40(1)
Co(2)	0	0	1282(1)	22(1)
P(2)	0	0	-825(1)	24(1)
C(22)	1279(2)	119(2)	-1574(2)	39(1)
C(12)	-1273(2)	1092(2)	875(2)	29(1)
B(32)	889(2)	1140(2)	2067(2)	30(1)
B(42)	-1504(2)	2274(2)	1454(2)	34(1)
B(52)	982(2)	2248(2)	242(2)	31(1)
B(62)	95(2)	1084(1)	150(1)	24(1)
C(72)	563(2)	1363(1)	2068(2)	30(1)
B(82)	303(2)	2457(2)	2229(2)	38(1)
B(92)	342(2)	3120(2)	1087(2)	37(1)
B(102)	551(2)	2364(2)	276(2)	31(1)
B(112)	1134(2)	1254(2)	958(2)	27(1)
B(122)	956(2)	2531(2)	1505(2)	35(1)

pairs of increase in the *wR*2 value from 8.90% to 11.47% for **1A** and from 7.53% to 10.15% for **1B**. The presented absolute configurations are therefore the best models for those crystal structures.

The differences in bond lengths among the four molecules in **1A** and **1B** (see Table 4) are within five standard deviations and within experimental error. However, the differences of bond lengths between enantiomers and racemic crystal are significantly larger. Those exceeding 7σ are marked by an asterisk in Table 4, all these different bonds involve at least one atom of the C_2B_3 circle. The C–B bonds are generally longer in **1R** than in **1A** and **1B** and, in contrast, the B–B bonds in **1R** are shorter. Also the range of the Co– bonds is smaller in **1R** [max (Co–X)−min (Co–X)=0.023 Å] than in **1A** and

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for **1B**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Co	0	0	-1280(1)	22(1)
P	0	0	827(1)	24(1)
C(2)	1275(2)	120(2)	1575(2)	40(1)
C(1)	-1273(2)	1095(1)	-873(1)	28(1)
B(3)	-884(2)	1137(2)	-2065(2)	31(1)
B(4)	-1503(2)	2269(2)	-1448(2)	35(1)
B(5)	-987(2)	2245(2)	-241(2)	32(1)
B(6)	-100(2)	1084(1)	-150(1)	24(1)
C(7)	565(2)	1364(1)	-2068(2)	30(1)
B(8)	-302(2)	2456(2)	-2228(2)	38(1)
B(9)	-342(2)	3121(2)	-1085(2)	37(1)
B(10)	549(2)	2364(2)	-273(2)	31(1)
B(11)	1130(2)	1262(2)	-955(2)	29(1)
B(12)	960(2)	2532(2)	-1505(2)	35(1)
Co(2)	5000	0	6274(1)	23(1)
P(2)	5000	0	4170(1)	24(1)
C(22)	6277(2)	119(2)	3419(2)	39(1)
C(12)	5992(2)	1324(1)	5870(1)	29(1)
B(32)	5593(2)	1278(2)	7062(2)	34(1)
B(42)	5926(2)	2518(2)	6451(2)	38(1)
B(52)	5446(2)	2398(2)	5239(2)	33(1)
B(62)	4853(2)	1084(1)	5150(1)	25(1)
C(72)	4124(2)	1217(2)	7058(2)	34(1)
B(82)	4706(2)	2452(2)	7222(2)	41(1)
B(92)	4595(2)	3114(2)	6086(2)	39(1)
B(102)	3911(2)	2199(2)	5261(2)	33(1)
B(112)	3597(2)	1000(2)	5939(2)	30(1)
B(122)	3468(2)	2282(2)	6498(2)	40(1)

1B (0.074 Å). Since some bond distances in **1R** are rather unusual such as B(11)–B(12)=1.738(4) Å, there is a possibility that these differences are due to those resulting from the disorder in the racemic crystal where an unequal occurrence of both enantiomers in the crystal can lead to averaging the C–B and B–B distances. Disorders in cage positions with the same effect on bond distances are usual in crystals with the *meta*-C_2B_9 cage, as was found in the Cambridge Structure Database[16] for the N,N′-dimethyltriethylenediammonium$^{(+)}$ [(1,7-$C_2B_9H_{11}$)$_2$-2-Ni]$^{(-)}$[17] and the racemic [6,6′-μ-pyrazolato-(1,7-$C_2B_9H_{11}$)$_2$-2-Ni] with a diatomic bridge,[18] see in files REFCODs: ETCBNI, YAHLOI.

2.2. *Nomenclature implications*

When an absolute configuration of any enantiomer is determined, there should be some unambiguous designations defining this particular species in terms of appropriate nomenclature. We met this problem for the first time many years ago and suggested an adequate solution.[19] In order to avoid ambiguity, the following rules should be obeyed for compounds of type **1**.

(i) Orient the bridging atom to the right as shown for **1A** in Fig. 5.
(ii) Only one icosahedron should be numbered, starting with C1 (neighbouring the bridgehead boron B6) and giving number 2 to the common Co-vertex.
(iii) Deploy the numbering spiral as it is conventional for any icosahedral heteroborane framework; right-hand deployment (clockwise)=σ-, left-hand deployment (anticlockwise)=ρ-.
(iv) Because in chiral compounds of this type the same procedure applied to the other ligand must give the same result, the designation σ- unequivocally defines one enantiomer, whereas ρ- defines its antipodal congener.
(v) In a *meso*-form, one ligand would be σ- and the other ρ-.

Table 4
Selected bond lengths [Å] and angles [°] for **1A**, **1B** and **1R**

Crystal	1A		1B		1R
Molecule	1	2	1	2	
Co-B(3)*	**2.058(2)**	**2.062(2)**	**2.056(2)**	**2.048(2)**	**2.079(3)**
Co-B(6)	2.067(2)	2.072(2)	2.071(2)	2.067(2)	2.066(3)
Co-C(1)	2.088(2)	2.078(2)	2.080(2)	2.084(2)	2.081(3)
Co-B(11)	2.095(2)	2.086(2)	2.091(2)	2.093(2)	2.081(3)
Co-C(7)*	**2.118(2)**	**2.120(2)**	**2.122(2)**	**2.121(2)**	**2.089(3)**
P-C(2)	1.802(2)	1.807(2)	1.803(2)	1.807(2)	1.804(3)
P-B(6)	1.923(2)	1.913(2)	1.914(2)	1.922(2)	1.915(3)
C(1)-B(6)*	**1.672(3)**	**1.687(3)**	**1.681(3)**	**1.674(3)**	**1.718(4)**
C(1)-B(4)*	**1.687(3)**	**1.699(3)**	**1.688(3)**	**1.694(3)**	**1.726(4)**
C(1)-B(5)*	**1.705(3)**	**1.720(3)**	**1.710(3)**	**1.718(3)**	**1.739(5)**
C(1)-B(3)	1.712(3)	1.708(3)	1.712(3)	1.712(3)	1.695(4)
B(3)-C(7)	1.696(3)	1.695(3)	1.692(3)	1.694(3)	1.689(4)
B(3)-B(8)*	**1.795(3)**	**1.790(3)**	**1.790(3)**	**1.799(3)**	**1.746(5)**
B(3)-B(4)*	**1.799(3)**	**1.795(3)**	**1.797(3)**	**1.804(3)**	**1.760(5)**
B(4)-B(8)	1.767(4)	1.764(4)	1.769(4)	1.766(3)	1.758(5)
B(4)-B(5)	1.772(3)	1.781(3)	1.773(3)	1.771(3)	1.775(5)
B(4)-B(9)	1.784(4)	1.779(3)	1.780(3)	1.777(4)	1.772(5)
B(5)-B(9)	1.772(3)	1.759(3)	1.764(3)	1.769(3)	1.771(5)
B(5)-B(6)	1.780(3)	1.780(3)	1.776(4)	1.779(3)	1.775(4)
B(5)-B(10)	1.800(4)	1.772(4)	1.776(3)	1.785(4)	1.775(5)
B(6)-B(10)	1.771(3)	1.770(3)	1.771(3)	1.771(3)	1.774(4)
B(6)-B(11)*	**1.810(3)**	**1.816(3)**	**1.815(3)**	**1.815(3)**	**1.754(4)**
C(7)-B(11)	1.683(3)	1.676(3)	1.677(3)	1.685(3)	1.684(4)
C(7)-B(8)*	**1.697(3)**	**1.705(3)**	**1.702(3)**	**1.694(3)**	**1.738(4)**
C(7)-B(12)*	**1.709(3)**	**1.713(3)**	**1.714(3)**	**1.712(3)**	**1.746(5)**
B(8)-B(12)	1.763(4)	1.765(3)	1.766(3)	1.755(4)	1.761(5)
B(8)-B(9)	1.784(4)	1.784(3)	1.786(3)	1.780(3)	1.779(5)
B(9)-B(12)	1.759(4)	1.763(4)	1.768(3)	1.757(4)	1.761(5)
B(9)-B(10)	1.801(3)	1.791(3)	1.792(3)	1.795(3)	1.775(5)
B(10)-B(12)	1.777(3)	1.775(3)	1.782(3)	1.789(3)	1.768(5)
B(10)-B(11)*	**1.790(3)**	**1.805(3)**	**1.796(3)**	**1.801(3)**	**1.759(4)**
B(11)-B(12)*	**1.769(3)**	**1.776(3)**	**1.769(3)**	**1.782(3)**	**1.738(4)**
C(2)$^{\#1}$-P-C(2)	109.9(2)°	110.0(2)°	109.9(2)°	109.8(2)°	110.3(2)°
B(6)$^{\#1}$-P-B(6)	90.30(12)°	90.3(1)°	90.2(1)°	90.3(1)°	90.3(2)°
Φ	8.23(3)°	8.84(3)°	8.60(3)°	8.19(3)°	8.45(6)°

Φ – dihedral angle between least-quare planes through circles C_2B_3 and $C_2^{\#1}B_3^{\#1}$.
* - distances with the large differences between **1A**, **1B** and **1R**.
Symmetry transformations used to generate equivalent atoms for **1A**,**1B** #1: 1-x,-y,z and for **1R**: -x+3/2,-y,z

In our case, the faster enantiomer **1A** is designated as ρ,ρ′-6,6′-μ-[$(CH_3)_2$P-(1,7-$C_2B_9H_{10}$)-2-Co], and its slower congener **1B** is the σ,σ′-μ-[$(CH_3)_2$P-(1,7-$C_2B_9H_{10}$)-2-Co] antipode.

Supplementary material comprising tables of observed and calculated structure factors and anisotropic thermal parameters of non-H atoms, Cambridge Structural Database search and data for related structures, and standard CIF files generated by SHELXL93 is available on request.

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References

1. J. Plešek, B. Grüner, J. Fusek, H. Votavová, *Collect. Czech. Chem. Commun.*, **1993**, *58*, 2936.
2. J. Plešek, B. Grüner, J. Holub, *Collect. Czech. Chem. Commun.*, **1997**, *62*, 884.
3. A. Franken, J. Plešek, J. Fusek, M. Semrau, *Collect. Czech. Chem. Commun.*, **1997**, *62*, 1070.
4. J. Plešek, A. Franken, R. Frölich, *Collect. Czech. Chem. Commun.*, **1997**, *62*, 57.
5. J. Plešek, B. Grüner, S. Heřmánek, J. Fusek, H. Votavová, *Collect. Czech. Chem. Commun.*, **1994**, *59*, 374.
6. J. Plešek, B. Grüner, T. Vaněk, H. Votavová, *J. Chromatogr.*, **1993**, *633*, 73.
7. B. Grüner, J. Plešek, The Dawn of Chirality in Deltahedral Boranes, in *Current Topics in the Chemistry of Boron*, ed. G. W. Kabalka, The Royal Society of Chemistry, Cambridge, 1994, pp. 371–374.
8. W. L. Hinze, T. E. Riehl, D. W. Armstrong, W. DeMond, A. Alak, T. Ward, *Anal. Chem.* **1985**, *57*, 237.
9. G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
10. G. M. Sheldrick, SHELXL93: A computer program for crystal structure refinement, University of Göttingen, Germany, 1993.
11. H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876–881.
12. J. Plešek, B. Grüner, P. Maloň, *J. Chromatogr.*, **1992**, *626*, 197.
13. J. Plešek, B. Grüner, P. Maloň, *Collect. Czech. Chem. Comunn.*, **1993**, *58*, 1087.
14. B. Grüner, J. Holub, J. Plešek, T. Vaňìk, H. Votavová, *J. Chromatogr. A.*, **1997**, in press.
15. R. A. Menges, D. W. Armstrong, in *Chiral Separations by Liquid Chromatography*, ed. S. Ahuja, Chapter 4, p. 69. ACS Symposium Series, American Chemical Society, Washington DC, 1991.
16. F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. Macrae, G. F. Mitchell, J. M. Smith, D. G. Watson, *J. Chem. Inf. Comp. Sci.*, **1991**, *31*, 187.
17. R. M. Wing, *J. Am. Chem. Soc.*, **1970**, *92*, 1187.
18. S. E. Varadarajan, S. E. Johnson, F. A. Gomes, C. B. Chakrabarti, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.*, **1992**, *114*, 9003.
19. J. Plešek, S. Heřmánek, B. Štíbr, *Collect. Czech. Chem. Commun.*, **1969**, *34*, 3233.