SYNTHESIS AND PROPERTIES OF (±)- AND (+)-4-MeS-3-C_2H_5-1,2,3-$C_2CoB_9H_{10}$

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Selective demethylation of the zwitterion 9-Me_2S-7,8-$C_2B_9H_{11}$ by sodium naphthalenide in tetrahydrofuran led to the racemic [9-MeS-7,8-$C_2B_9H_{11}$]$^-$ ion, which could be partially resolved to its (−)-enantiomer via the [(−)-1-Ph-1-Me_3N-$CHCH_3$]$^+$ salt. Complexation of the ions with Co^{2+} and $C_5H_5^-$ afforded the (±)- and (+)-4-MeS-3-C_5H_5-1,2,3-$C_2CoB_9H_{10}$ cobaltacarboranes, respectively. A partially resolved (−)-9-Me_2S-7,8-$C_2B_9H_{11}$ was obtained by re-methylation of the (−)-[9-MeS-7,8-$C_2B_9H_{11}$]$^-$ ion.

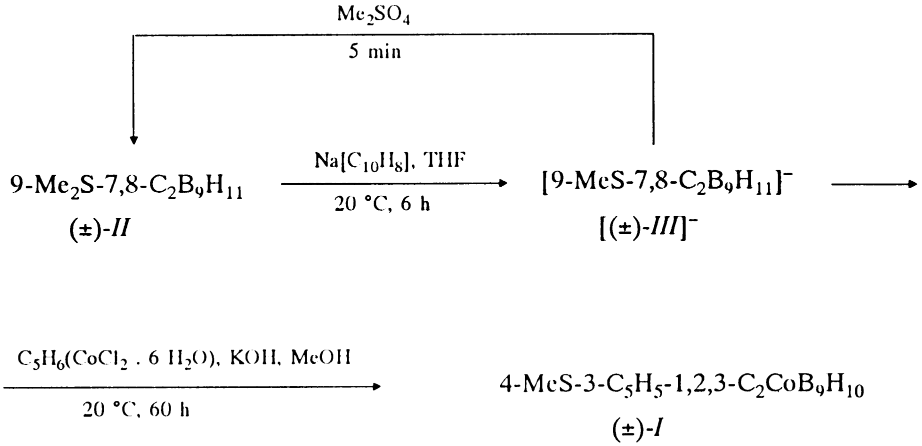
Up to now only about 20 well characterized chiral species with deltahedral borane cages have been reported[1]. In order to improve this bleak situation we decided to adapt the HPLC resolution on chiral recognition columns for this class of compounds. Among the first deltahedral borane derivatives successfully resolved to enantiomers by HPLC method using chiral β-cyclodextrin bonded stationary phase[2] was the 4-MeS-3-C_2H_5-1,2,3-$C_2CoB_9H_{10}$ ((±)-*I*) cobaltacarborane (Fig. 1). Here we report on synthesis and some properties of this hitherto not described species and of its (+)-enantiomer.

RESULTS AND DISCUSSION

On treatment of the easily accessible[3] zwitterion 9-Me_2S-7,8-$C_2B_9H_{11}$ ((±)-*II*) with metallic sodium in THF with naphthalene as electron transfer catalyst one Me^+ ion from the Me_2S^+-moiety becomes split off leaving the [9-MeS-7,8-$C_2B_9H_{11}$]$^-$ ion [(±)-*III*]$^-$ (Fig. 2). Two electrons necessary for transformation $Me^+ \rightarrow Me^-$ are apparently provided by two sodium atoms. This interesting demethylation might be quite general with deltahedral zwitterions containing a dimethyl sulfide ligand.

Treatment of [(±)-*III*]$^-$ with Co^{2+} and $C_5H_5^-$ ions in concentrated ethanolic alkali hydroxide solutions[4] caps the pentagonal open face of the ion [(±)-*III*]$^-$ with a cyclopentadienylcobalt-vertex under formation of the desired cobaltacarborane (±)-*I* (Scheme 1).

The smooth demethylation of (±)-*II* (ref.[3]) led to the hitherto unknown [(±)-*III*]$^-$ ion in high yield. Re-methylation to the starting zwitterion was smooth and quantitative, indicating that no structural change complicated the demethylation.



SCHEME 1

Synthesis of the sandwich (±)-*I* has been carried out via our "alcoholic route" (ref.[4]) because the classical "aprotic route" (ref.[5]) failed in this case. Genesis of *I* and *III* leaves no doubt on respective constitutions, well supported also by the NMR data (see Experimental).

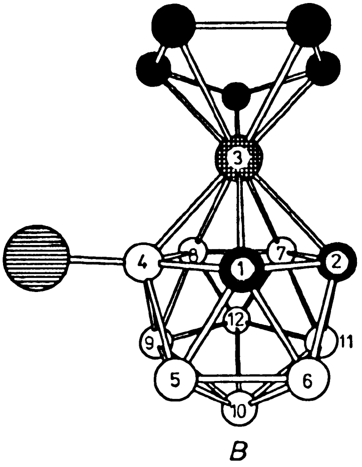


FIG. 1

Icosahedral $4\text{-}MeS\text{-}3\text{-}C_5H_5\text{-}1,2,3\text{-}C_2CoB_9H_{10}$ ((±)-*I*). For clarity, the terminal hydrogen atoms are omitted. The void point B, the full point C, the point with cross-hatching Co, the point with horizontal hatching SCH_3

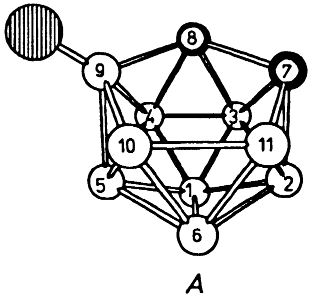


FIG. 2

$[9\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]^-$ ion ([±)-*III*]⁻). For clarity, the terminal hydrogen atoms and hydrogen bridge are omitted. Hydrogen bridge is positioned between 10 and 11 boron atoms. The void point B, the full point C, the point with vertical hatching SCH_3

A threefold recrystalization of the semisolid [(±)-*III*] . [(–)-TMPA] salt ([(–)-TMPA$^+$] = (–)-[1-Ph-1-Me_3N-$CHCH_3$]$^+$ ion) from 50% ethanol afforded snow-white needles of the partially resolved [(–)-*III*] . [(–)-TMPA] salt, m.p. 89 – 90 °C. There was no intention to crystallize this product to an ultimate optical purity, neither to isolate the other enantiomer from the mother liquors.

Conjugate acid [(–)-*III*]$^-$. [H_3O]$^+$ has been set free from the salt with the auxiliary counterion by conventional diethyl ether–hydrochloric acid treatment[6]; from an aliquot the [(–)-*III*] . Cs salt was precipitated for evaluation of optical properties of the salt (Fig. 3). The remaining solution of the acid was neutralized to [(–)-*III*] . Na salt and converted to the ((+)-*I*) sandwich as was done before with racemic [(±)-*III*]$^-$ ion. The so obtained ((+)-*I*) showed a 32% enantiomeric excess (e.e.) of the dextrorotary enantiomer as assessed elsewhere[2] by HPLC with chiral β-cyclodextrin column. Its CD curve is shown on Fig. 4. Presuming that no racemization occurred during its synthesis from the original [(–)-*III*]$^-$ ion we can assume the e.e. of this ion was also about 32%.

It is probably the first well characterized optically active deltahedral sandwich complex ever reported. Both enantiomers of rhodacarborane complex briefly mentioned in a Russian note[7] were not characterized by any adequate method and their structures and optical purity are dubious.

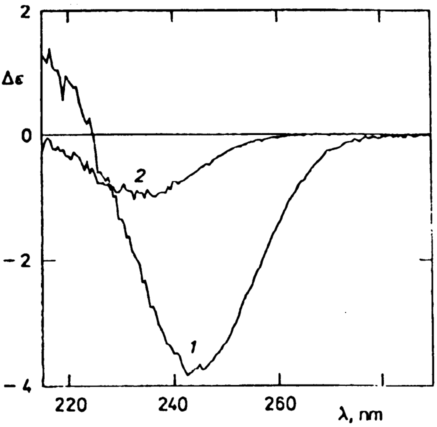


Fig. 3

Circular dichroism spectra of (–)-9-MeS-7,8-$C_2B_9H_{11}$. Cs (*1*), (–)-9-Me_2S-7,8-$C_2B_9H_{11}$ (*2*)

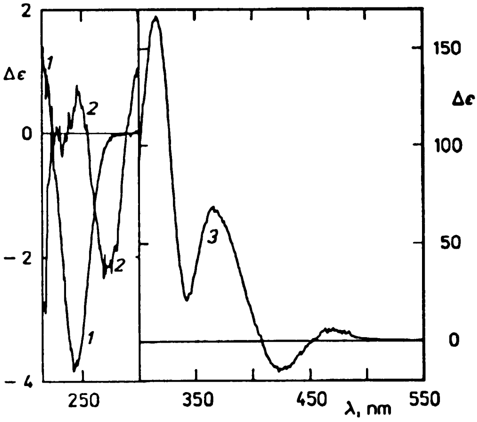


Fig. 4

Circular dichroism spectra of (–)-9-MeS-7,8-$C_2B_9H_{11}$. Cs (*1*); (+)-4-MeS-3-C_5H_5-1,2,3-$C_2CoB_9H_{10}$, short wavelength region (*2*); (+)-4-MeS-3-C_5H_5-1,2,3-$C_2CoB_9H_{10}$, long wavelength region (*3*)

Methylation of the [(–)-*III*]$^-$ ion regenerated from synthesis of ((+)-*I*) afforded the hitherto unknown ((–)-*II*) zwitterion apparently with the same e.e. of 32%. its CD curve is shown in Fig. 3.

EXPERIMENTAL

The NMR spectra (δ, ppm) were measured with Varian XL-200 spectrometer at 200 MHz (^{1}H) and 64.18 MHz (^{11}B) in deuterioacetone (relative to $BF_3 . OEt_2$ as internal standard –18.2 ppm). Mass spectra were recorded with Jeol HP-5985 by electron impact ionization at 70 eV. Circular dichroism spectra were recorded on Auto Dichrographe Mark V (Jobin Yvon, France), driven by a microcomputer (Silex, France) loaded with our own software. The measurements were executed in acetonitrile (Uvasol, Merck) at concentrations 1.5 – 3.0 . 10^{-3} mol l^{-1} in quartz cells with the optical path length 0.02 – 0.1 cm. The spectra are computer averages over 2 – 3 instrument scans and the data are presented as ε values. Specific rotations were measured on Perkin–Elmer 241 polarimeter in 5 cm tube in acetonitrile. TLC has been carried out on Silufol (Kavalier Votice, The Czech Republic). Commercial chemicals and solvents were of reagent grade; the compound ((±)-*II*) has been prepared according to ref.[3]. All operations have been carried out under anaerobic conditions.

Demethylation of 9-Me_2S-7,8-$C_2B_9H_{11}$ to [9-MeS-7,8-$C_2B_9H_{11}$]$^-$ Ion ((±)-*III*)

In a 250 ml flask immersed into a cooling bath (water, 20 °C) and fitted with a magnetic stirring bar, a mixture of 7.7 g (0.04 mol) of (±)-*II*, 0.65 g (0.005 mol) of naphthalene and 2.3 g (0.1 mol) of sliced sodium in 80 ml of THF was gently stirred for 6 h until a probe showed no presence of starting zwitterion (TLC). Metallic sodium gradually dissolved and the solution turned deep brown. The remaining sodium was removed, the solution was poured into 200 ml of water and THF was stripped off in a rotary evaporator in vacuum. The turbid solution was extracted twice with 20 ml of hexane and the aqueous solution was concentrated to 100 ml volume; from 20 ml of this solution, the cesium salt was precipitated by 2.0 g of CsF in 10 ml of water and the precipitate was dissolved by addition of 50 ml of water and heating to 80 °C. On cooling overnight fluffy needles of [(±)-*III*]. Cs salt separated; 2.35 g (90%); ^{1}H NMR spectrum: 1.62 + 2.90 ppm (CH carborane), 2.05 ppm (finely split quartet of the MeS- group) and –2.56 ppm (broad B–H–B bridge). ^{11}B NMR spectrum: +1.21 (s, 1), –10.34 (1), –13.82 (1), –18.00 (1), –21.69 (1), –23.23 (2), –32.52 (1), –37.97 (1).

Re-methylation of the [9-MeS-7,8-$C_2B_9H_{11}$]$^-$ Ion

To another 5 ml portion of the above aqueous solution of [*III*] . Na salt (0.2 mmol) 0.5 g of K_2CO_3 in 10 ml of water was added, followed by 0.6 g of dimethyl sulfate (5 mmol). The mixture was vigorously shaken for 5 min, 5 ml of 15% aqueous ammonium hydroxide was added to destroy the excess dimethyl sulfate and after 5 min of shaking the product was extracted into 20 ml of chloroform; a TLC chromatogram showed only the spot of (±)-*II*, R_F 0.20 (benzene). Evaporation of the filtered chloroform extract afforded 0.36 g (94%) of (±)-*II* as white crystalline powder, m.p. 147 – 148 °C (ref.[3] m.p. 147 – 148 °C).

Synthesis of (±)-4-MeS-3-C_2H_5-1,2,3-$C_2CoB_9H_{10}$ ((±)-*I*)

In a rotary evaporator the remaining 80 ml of the above aqueous solution of the [(±)-*III*] . Na salt (0.03 mol) was concentrated to 10 g of viscous oil. This was dissolved in 30 ml of ethanol and 10 ml freshly distilled cyclopentadiene was added. The resulting turbid solution was poured in a viscous slurry prepared from 12.5 g (0.05 mol) of $CoCl_2 . 6 H_2O$ in 60 ml of ethanol by addition of 30 g of KOH pellets followed by vigorous shaking for 5 min under cooling with water. Magnetic stirrer was inserted afterwards and the mixture was stirred for 60 h at room temperature. A short evacuation removed excess of cyclopentadiene and the reaction mixture was poured into 500 ml of cold water. Ethanol was stripped off in vacuum and remaining slurry was saturated with CO_2. The solids were filtered off and extracted three times with 50 ml of acetone. Deep orange extracts were combined and acetone was stripped off in vacuum. The residue was successively extracted three times with 30 ml portions of benzene and the benzene extracts were gradually soaked into a 200 g of dry silica gel column (diameter 3 cm). The lemon-yellow band of the product was eluted with benzene. Eluates were evaporated in vacuum and the residue was crystallized from 80 ml of boiling ethanol. After standing for 70 h the deep orange prisms were filtered off and dried in ambient atmosphere; 3.64 g (40%), m.p. 218 – 219 °C. Mass spectrum (*m/z*): 304 (for $^{12}C_8{}^1H_{18}{}^{11}B_9{}^{32}S^{59}Co$ calculated: 304), 59 (Co^+), 124 ($C_5H_5Co^+$). TLC: R_F 0.18 (benzene). ^1H NMR spectrum: 1.94 (MeS), 4.77 + 4.52 (CH carborane), 5.8 (cyclopentadiene). ^{11}B NMR spectrum: +6.74 ppm (1 + 1), +0.30 (1), −5.54 (1), −7.18 (2), −16.12 (1), −20.02 (1), −22.74 (1).

Partial Resolution of $[(\pm)\text{-}III]^-$ to $[(-)\text{-}III]^-$

Demethylation of 3.85 g (0.02 mol) of (+)-*II* to (+)-*III* has been carried our as above. The final aqueous solution of the [(±)-*III*] . Na salt was precipitated with 7.3 g (0.025 mol) of [(−)-1-Ph-1-Me$_3$N-CHCH$_3$] . *I* (ref.[8]) ((−)-TMPEA) in 60 ml of water. The semi-solid matter solidified overnight and crystallized three times from 100 ml of 50% aqueous ethanol. Only the snow-white needles of the [(−)-*III*] . [(−)-TMPEA] salt from the last crystallization were isolated, (2.54 g, 75%), m.p. 89 – 90 °C (crude diastereomeric salt [(+)-*III*] . [(−)-TMPEA] from the first mother liquors showed m.p. 69 °C).

Suspension of [(−)-*III*] . [(−)-TMPA] salt in 50 ml of diethyl ether and 15 ml of 15 % hydrochloric acid was stirred until all solids disappeared, the ether layer containing the conjugate acid [(−)-*III*] . [H_3O] . *n* H_2O was neutralized with excess of 15% sodium carbonate and the ether layer was separated again. After addition of the same volume of water ether was stripped off in vacuum, leaving aqueous solution of [(−)-*III*] . Na salt. Its volume was adjusted to 37.5 ml to give approximately 0.2 M solution.

The respective Cs salt was precipitated from 7.5 ml of this solution and recrystallized from hot water; long white needless, $[\alpha]_D^{25}$ −15.84° (*c* 0.45, acetonitrile). CD curve is shown in Fig. 3.

The remaining 30 ml of the 0.2 M solution of [(−)-*III*] . Na salt was concentrated in vacuum to a thick syrup and treated with cyclopentadiene–$CoCl_2$. 6 H_2O–EtOH–KOH mixture as described above with (±)-*I*. In this case, however, from the aqueous filtrate after separation of the crude (+)-*I* the unreacted [(−)-*III*] . K salt was regenerated for re-methylation to (−)-*II* (see below). Crude (+)-*I* was purified by column chromatography as described above with (±)-*I*. However, final crystallization of the eluted (+)-*I* from ethanol was not carried out in this case in order to avoid a change of the ratio (+)-*I*/(±)-*I*. Benzene from the yellow eluate was stripped off in vacuum, leaving a crystalline orange powder of (+)-*I*, 0.74 g (41%), m.p. 208 °C (racemate melts at 218 – 219 °C). TLC: R_F 0.18 (benzene). Mass spectrum: 304. $[\alpha]_D^{25}$ +38.34° (*c* 0.32, acetonitrile). CD curve is shown in Fig. 4. According to HPLC analysis on the chiral β-cyclodextrin column[2] the compound showed 32% e.e. of dextrorotary enantiomer.

The water filtrate after isolation of the crude (+)-*I* was extracted three times with 50 ml of diethyl ether; from the combined diethyl ether extracts, ether was stripped off in vacuum leaving an aqueous solution of regenerated [(−)-*III*] . K salt, identified by TLC as essentially pure. Treatment of this solution with 1 ml of dimethyl sulfate as described above with (±)-*II*, afforded 0.37 g (32%) of the partially resolved (−)-*II*, m.p. 147 – 148 °C, $[\alpha]_D^{25}$ −8.70° (*c* 0.45, acetonitrile). TLC: R_F 0.20 (benzene). Mass spectrum (*m/z*): 196. CD curve is shown in Fig. 3.

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