

FOUR NEW $(\text{CH}_3)_2\text{S}\cdot\text{C}_2\text{B}_9\text{H}_{11}$ ISOMERS

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Czechoslovak Academy of Sciences, 250 68 Řež**Dedicated to Professor F. Čůta on the occasion of his 80th birthday.*

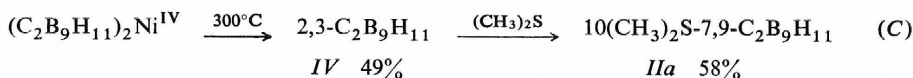
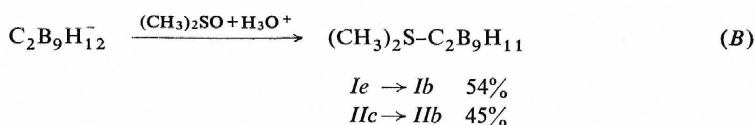
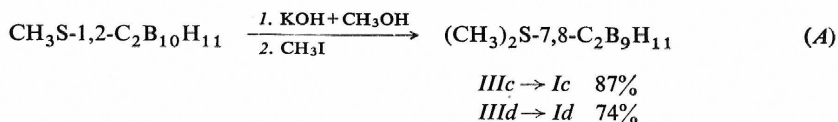
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A selective degradation followed by methylation transformed $1\text{-CH}_3\text{S-}$ and $9\text{-CH}_3\text{S-1,2-C}_2\text{B}_{10}\cdot\text{H}_{11}$ to the $7(\text{CH}_3)_2\text{S-}$ and $5(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ derivatives. Further two isomers, $9(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ and $8(\text{CH}_3)_2\text{S-7,9-C}_2\text{B}_9\text{H}_{11}$ were obtained by a reaction of the $7,8\text{-}$ and $7,9\text{-C}_2\text{B}_9\text{H}_{12}\text{-}$ anions with dimethyl sulfoxide. Similarly, the $(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Co}^-$ anion was transformed to the uncharged $8(\text{CH}_3)_2\text{S-1,2-C}_2\text{B}_9\text{H}_{10}\text{-3-Co-1,2-C}_2\text{B}_9\text{H}_{11}$ ligand derivative. The reaction of the $2,3\text{-C}_2\text{B}_9\text{H}_{11}$ carborane with $(\text{CH}_3)_2\text{S}$ gave $10(\text{CH}_3)\text{S-7,9-C}_2\text{B}_9\text{H}_{11}$. Structures of all derivatives were derived from the ^{11}B and $^1\text{H-NMR}$ data.

A family of isomers of the general formula $(\text{CH}_3)_2\text{S}\cdot\text{C}_2\text{B}_9\text{H}_{11}$ has theoretically 71 members if only positions of both C-skeletal atoms and of a ligand are considered in the eleven vertex fragment of an icosahedron. All these compounds are isoelectronic and isostructural with the appropriate $\text{C}_2\text{B}_9\text{H}_{12}^-$ anion (9 isomeric anions). From this extensive series, only two representatives are known¹, namely $10(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ (*Ia*) and $9(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ (*Ib*) in which the ligand is bound to the B-atoms in the open pentagonal face, *i.e.* to the atoms with coordination number 5.

We have now found a route to the synthesis of four further isomers: $7(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ (*Ic*), $5(\text{CH}_3)_2\text{S-7,8-C}_2\text{B}_9\text{H}_{11}$ (*Id*), $10(\text{CH}_3)_2\text{S-7,9-C}_2\text{B}_9\text{H}_{11}$ (*Ila*), and $8(\text{CH}_3)_2\text{S-7,9-C}_2\text{B}_9\text{H}_{11}$ (*Iib*). The isomer *Ic* is a first representative of this family having an uncharged ligand on a C-atom while the isomer *Id* is a first member in the $7,8\text{-C}_2\text{B}_9\text{H}_{11}\text{L}$ series with a ligand located out of the open face of the molecule, *i.e.* bound to atoms with the coordination number 6. A comparison of the isomer couple *Ia*, *Ib* with that of *Ila*, *Iib* has shown that the former corresponds to the $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion (*Ie*) while the latter corresponds to the $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion (*Iic*), as followed from their chemical origin. This demonstrates that during the ligand introduction no change in positions of C-atoms occurs. A possibility of such an isomerism was not excluded by Grimes² in his book when speaking on preparation of analogs with other ligands described in^{3,4}.

Synthesis of particular compounds is evident from the following schemes:

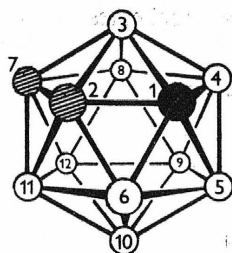


The synthesis of the *closo*-carborane $2,3\text{-C}_2\text{B}_9\text{H}_{11}$ (*IV*) according to the Scheme (C) is still the easiest route on which this carborane can be prepared. Previously described alternatives are appreciably more complicated and afford lower yields^{3,5,6}. In the product of thermolysis (C) also $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ (16%), $(\text{C}_2\text{B}_9\text{H}_{10})_2$ (4%) and $1,2\text{-C}_2\text{B}_8\text{H}_{10}$ (2%) were identified besides the main product *IV*. These by-products can be easily separated by sublimation at 1.3 Pa (0.01 Torr) and at room temperature, when only practically pure $2,3\text{-C}_2\text{B}_9\text{H}_{11}$ (*IV*) volatilizes. In the polymeric residue, all Ni and almost exactly half of original contents of B and C remains. This mass is a black glass, insoluble in all common solvents. For a high yield of carborane *IV* the volatile products have to be continuously removed. The thermolysis in a closed system⁷ affords, namely, a mixture containing isomers of the starting metallocarborane, accompanied by carboranes $\text{C}_2\text{B}_7\text{H}_9$, $\text{C}_2\text{B}_9\text{H}_{11}$ and $(\text{C}_2\text{B}_9\text{H}_{10})_2$.

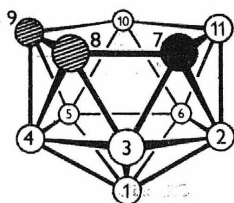
Properties of compounds *Ic*, *Id*, *IIa*, *IIb*, and compound *Ib* prepared on a new way (Scheme B) are shown in Tables I and II. In the Tables there are given for comparison also NMR characteristics of *Ia* and of the both $\text{C}_2\text{B}_9\text{H}_{12}^-$ anions (*Ie*, *IIc*).

Constitution of new derivatives *Ic*, *Id*, *IIa* and *IIb* resulted from their chemical origin and from the analysis of their ^{11}B and ^1H -NMR spectra. A close relationship of isomers *Ib*, *Ic* and *Id* with the $7,8\text{-C}_2\text{B}_9$ *nido*-series is evident from a distinct secondary splitting of the signal at 25.8 (with *Ib*), 30.2 (*Ic*) and 32.6 ppm (*Id*) which is also present with the $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion at 33.4 ppm⁸ and is caused by the presence of a hydrogen bridge, located between atoms $\text{B}_{(9-10)}$ or $\text{B}_{(10-11)}$, *i.e.* interacting always with the $\text{B}_{(10)}$.

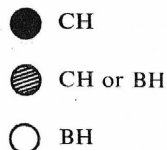
Compounds *IIa* and *IIb* can be classified as members of the $7,9\text{-C}_2\text{B}_9$ series because both have in their ^{11}B -NMR spectrum a specific very narrow signal (singlet at 4.9 with *IIb*, doublet at 4.5 ppm with *IIa*) which is also present with the $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ anion (at 6.2 ppm), and is characteristic of the B-atom located between two heteroatoms in an open face⁹, *i.e.* of the $\text{B}_{(8)}$ atom in the $7,9\text{-C}_2\text{B}_9$ *nido*-skeleton.



III, 1,2-C₂B₉H₁₁X
 IIIc, X = 1-CH₃S
 IIId, X = 9-CH₃S



I, 7,8-C₂B₉H₁₁L
 Ia, L = 10(CH₃)₂S
 Ib, L = 9(CH₃)₂S
 Ic, L = 7(CH₃)₂S
 Id, L = 5(CH₃)₂S
 Ie, L = H
 II, 7,9-C₂B₉H₁₁L
 IIa, L = 10(CH₃)₂S
 IIb, L = 8(CH₃)₂S
 IIc, L = H



The position of the (CH₃)₂S-group, expected from the chemical preparation is with isomers *Ic*, *Id* and *IIf* in a good agreement both with the location of a ¹¹B-NMR signal of the substituted atom and with the general character of the particular ¹¹B-NMR spectra (Table II). With the isomer *IIa*, an overlap of signals in the critical area of 19–21 ppm does not allow to deduce whether the ligand is in position B₍₃₎ or B₍₁₀₎. The ¹¹B-NMR spectrum of *IIa* is, however, very similar to that

TABLE I
 Some Characteristic of the (CH₃)₂S·C₂B₉H₁₁ Derivatives (*m/e* in all cases 196)

Isomer	Position of ligand	M.p., ^a °C	R _F ^b	¹ H-NMR ^c			
				C—H	B—H—B	CH ₃	Solvent ^d
<i>Ia</i>	10			2·22	—1·17	2·55	C
<i>Ib</i>	9	147—148	0·21	2·22	—3·37	2·62	C
				2·70	2·80		
<i>Ic</i>	7	260—263 ^e	0·02	2·36	—2·77	3·00	A
					3·04		
<i>Id</i>	5	54—55	0·44	2·15	—2·40	2·50	C
<i>IIa</i>	10	71 ^e	0·21	1·50	—2·05	2·72	A
<i>IIb</i>	8	97—98	0·11	1·75	—2·20	2·75	A

^a Not corrected, sealed capillary; ^b TLC on Silufol (silica gel on aluminium foil), benzene; ^c ppm relative to tetramethylsilane; ^d C = CDCl₃, A = CD₃COCD₃; ^e decomposition.

of 10-L-7,9- $\text{C}_2\text{B}_9\text{H}_{11}$ derivative¹⁰ which was prepared analogously by an addition of $\text{L} = \text{CH}(\text{CN})_2^-$ to 2,3- $\text{C}_2\text{B}_9\text{H}_{11}$. This is why we propose for *Ila* the 10- $(\text{CH}_3)_2\text{S}\cdot\text{C}_2\text{B}_9\text{H}_{11}$ structure.

Analyses of particular NMR spectra indicate that the expected compounds resulted in all preparations and in no case an isomerization occurred. With isomers *Ib* and *Ic*, signals of two non-equivalent CH_3 -groups have been observed, which indicates that there is no free rotation of the $(\text{CH}_3)_2\text{S}$ -ligand around the B—S bond.

All compounds of the general formula $\text{L}\cdot\text{C}_2\text{B}_9\text{H}_{11}$ are potential precursors of the sandwich-generating $\text{L}\cdot\text{C}_2\text{B}_9\text{H}_{10}^-$ anions which are in this meaning fully equivalent to the cyclopentadienyl anion. An ability of these species to form sandwich compounds was proved with easily accessible isomer *Ib* which reacts with cobaltous salts in the presence of the $\text{C}_2\text{B}_9\text{H}_{12}^-$ anion even in an aqueous medium according

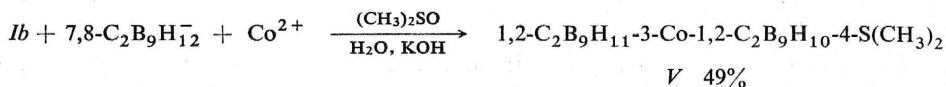
TABLE II

¹¹B-NMR Signals of Dimethyl Sulfide Derivatives and of the 7,8- $\text{C}_2\text{B}_9\text{H}_{12}^-$ and 7,9- $\text{C}_2\text{B}_9\text{H}_{12}^-$ Anions (32.1 MHz, ppm relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$)

Compound (pos. of ligand)	Solvent ^a	Intensity, ppm (assignment)					
7,8- $\text{C}_2\text{B}_9\text{H}_{12}^-$	A	11.2 (9,11)	17.5 (3; 5,6)	22.4 (2,4)	33.4 ^b (10)	38.0 (1)	
<i>Ia</i> (10-L)	M + B	10.3 (9,11)	16.1 (5,6)	16.7 (3)	20.5 (2,4)	26.0 ^c (10)	37.4 10
<i>Ib</i> (9-L)	A	2.6 3.2 ^c (9)	9.7 13.4	14.8	19.3 22.1	25.8 ^b (10)	34.2 (1)
<i>Ic</i> (7-L)	A	9.9 [2]	10.9 14.6	18.8 [2]	21.3	30.2 ^b (10)	32.2 (1)
<i>Id</i> (5-L)	C	9.0 14.0 ^c (5)	14.0 [2]	17.4	22.1 23.2 (2,4)	33.6 ^b (10)	38.9 (1)
7,9- $\text{C}_2\text{B}_9\text{H}_{12}^-$	A	5.3 (2,5)	6.1 ^d (8)	22.1 (3,4)	23.1 ^b (10,11)	35.4 (6)	35.4 (1)
<i>Ila</i> (10-L)	A	1.5 72.5 (2,5)	4.5 ^d (8)	13.5 ^c (10)	19.5 ^b (11)	20.4 (3,4)	32.7 (6,1)
<i>Ilb</i> (8-L)	A	4.7 (2,5)	4.9 ^{c,d} (8)	21.2 (3,4)	21.8 ^b (10,11)	33.6 (6)	34.0 (1)

^a A = CD_3COCD_3 , M = CH_2Cl_2 , B = C_6D_6 , C = CDCl_3 ; ^b $J_{\text{B}\mu\text{H}}$ 30—45 Hz; ^c singlet; ^d narrow signal.

to the scheme:



The orange uncharged complex *V* has not yet been described. The central Co atom reached its formal oxidation number 3+ on account of a part of Co^{2+} ions which were reduced to the elemental Co.

EXPERIMENTAL

Starting 1-HS-1,2- $C_2B_{10}H_{11}$ was prepared according to¹¹, the synthesis of 9-HS-1,2- $C_2B_{10}H_{11}$ has been described by us recently^{12,13}. Mass spectra were determined with a LKB 9000 instrument at 70 eV. The 1H (100 MHz) and ^{11}B (32.1 MHz) NMR spectra were recorded using a Varian XL-100 spectrometer. Melting points were measured in a Koffler block and are uncorrected. TLC was carried out on Silufol (silica gel on Al foil; Kavalier, Votice, Czechoslovakia).

Preparation of Isomers *Ib* and *Iib*

Dimethyl sulfoxide (15.6 g, 0.2 mol) was added to 50 ml of 1M aqueous solution of $C_2B_9H_{12}K$ and to this mixture 50 ml of conc. sulfuric acid were added dropwise under cooling below 30°C. A two-layer mixture was left to stand overnight, then it was diluted with 200 ml of water, and a solid product was sucked off and recrystallized. The isomer *Ib* was recrystallized from 80% methanol; needle-shaped prisms, 5.2 g (53.6%). The isomer *Iib* was recrystallized from benzene-cyclohexane 1 : 1; needles, 4.35 g (44.7%).

Preparations of Isomers *Ic* and *Id*

Potassium hydroxide (16 g) was dissolved in 100 ml of methanol and after cooling the solution to room temperature 7.0 g (0.04 mol) of 1-HS-1,2- $C_2B_{10}H_{11}$ (or 9-HS-1,2- $C_2B_{10}H_{11}$) was added. To the resulting mixture was added 6.5 g (0.04 mol) of methyl iodide. After 5 minutes, TLC analysis of the mixture showed only spots of appropriate methylthio ethers which could be isolated in a high yield in this stage. The reaction mixture was then refluxed until the end of hydrogen evolution (1 hour with *Ic*, 5 hours with *Id*). In this stage no presence of methylthio ethers was observed by TLC. After cooling to an ambient temperature 10 ml of methyl iodide were added, the mixture was left to stand for 30 minutes, the excess methyl iodide was evaporated in vacuo together with a part of methanol and the distillation residue was diluted with 200 ml of water. With isomer *Ic*, the separated product was filtered and recrystallized from hot 80% methanol; prisms, 6.77 g (87.2%). In the case of isomer *Id*, the product was extracted into benzene, benzene layer was washed with water, reduced *in vacuo* to a volume of 10 ml and the benzene solution was cautiously covered with 30 ml of hexane. By standing overnight a solid product *Id* (3.77 g, 74.7%) separated.

Preparation of Isomer *Iia*

To 4.8 g (0.03 mol) of freshly sublimed carborane $C_2B_9H_{11}$ (see below) was added 20 ml of dimethyl sulfide under cooling to room temperature. The mixture was left to stand for 4 days,

dimethyl sulfide was evaporated *in vacuo* and a residue was shaken with a mixture of 30 ml of benzene and 30 ml of water. Benzene extract was washed with 2.30 ml of 5% potassium hydroxide, filtered, reduced *in vacuo* to a volume of 10 ml and covered with 30 ml of hexane. By standing overnight, product *Ila* crystallized in the form of white needles; 3.35 g (57.7%). Isomer *Ila* cannot be distinguished by TLC from *Ib* but both differ distinctly in their ^1H and ^{11}B -NMR spectra and in thermal stability. While the isomer *Ib* can be dried at 100°C in air, the isomer *Ila* begins to fume at 50°C and smells of a characteristic odour of the starting $\text{C}_2\text{B}_9\text{H}_{11}$ carborane.

Preparation of Carborane 2,3- $\text{C}_2\text{B}_9\text{H}_{11}$ (*IV*)

Complex compound $(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Ni(IV)}$ (19.2 g, 0.06 mol) was heated over 300°C in a nitrogen atmosphere. Over 200°C the complex gradually sintered, melted and turned orange-brown. Simultaneously, yellowish crystals of the product *IV* appeared in air reflux condenser. The mixture was heated for 6 hours, left to cool to room temperature and the crude carborane was sublimed off at 1.3 Pa (0.01 Torr) and at ambient temperature from the reaction flask to the cooling finger containing dry ice and methanol. Characteristically smelling carborane 2,3- $\text{C}_2\text{B}_9\text{H}_{11}$ (7.80 g, 49.2%) was obtained. Its mass, ^1H and ^{11}B -NMR spectra were identical with those reported in⁶. The sublimation residue consisted of synthesis by-products, which were *o*-carborane (6%), 1,2- $\text{C}_2\text{B}_8\text{H}_{10}$ (2%), and dimer $(\text{C}_2\text{B}_9\text{H}_{10})_2$ (4%, *m/e* 266). The by-products were identified by a combination of GLC and mass spectroscopy. On the bottom of the sublimation flask, 11.1 g of a brittle black glass remained. All attempts to dissolve this glass in organic solvents or to decompose it in an acetone-HCl (1 : 1) mixture were unsuccessful.

Synthesis of Complex *V*

To 10 ml of 1M aqueous solution of 7,9- $\text{C}_2\text{B}_9\text{H}_{12}\text{K}$ were added compound *Ib* (2.0 g, 0.01 mol), dimethyl sulfoxide (10 ml) and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (5.0 g, 0.02 mol). When the solid phase dissolved, two layers separated. Potassium hydroxide (6 g), was added to the mixture which warmed spontaneously and turned brown-black. A pasty mass was heated for 1 hour on a boiling water bath, then it was diluted with 100 ml of water and solid species were sucked off. The residue on a filter was washed with 30 ml of water and 3.10 ml benzene, leaving a red powder, sparingly soluble in benzene. The powder was dissolved in acetone, the solution was filtered, 100 ml of benzene were added and acetone was evaporated slowly *in vacuo*. Product *V* separated in the form of orange needles; 1.88 g (49.1%), m.p. $320\text{--}325^\circ\text{C}$ (dec.), R_f 0.30 (Silufol, benzene), *m/e* 388 in accord with the calculated isotopic mass. The ^{11}B -NMR spectrum exhibited doublets (intensities) at -8.61 (1), -6.6 (1), 0.90 (1), 3.5 (3), 6.1 (1), 8.07 (3), 14.43 (2), 16.54 (2), 20.1 (1), 21.0 ppm (1) and a singlet at -7.44 ppm (1). The character of this spectrum is consistent with the proposed constitution of *V*.

The ^{11}B -NMR spectra were measured by Mr P. Pech, the mass spectra by Dr J. Mitera, Prague Institute of Chemical Technology, Prague. The ^1H -NMR spectra were recorded by Dr F. Mareš, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. We would like to express our thanks to these colleagues for their assistance.

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