

ZWITTERIONIC COMPOUNDS OF THE 8,8'-X(C₂B₉H₁₀)₂Co SERIES
WITH MONOATOMIC O, S, Se, Te, N BRIDGES
BETWEEN CARBORANE LIGANDS

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The sandwich-like (C₂B₉H₁₁)₂Co⁻ anion reacts with RCHO in H₂SO₄ with formation of the zwitterionic 8,8'-RCH₂O(C₂B₉H₁₀)₂Co compounds with carborane ligands bound by a RCH₂O bridge. In a similar reaction with SeO₂, Te, or NaNO₂, the bridged 8,8'-Se(C₂B₉H₁₀)₂Co⁽⁻⁾, 8,8'-Te(C₂B₉H₁₀)₂Co⁽⁻⁾ or 8,8'-H₂N₂(C₂B₉H₁₀)₂Co compounds arise which can be methylated to the zwitterionic 8,8'-X(C₂B₉H₁₀)₂Co compounds (X = CH₃Se, CH₃Te, (CH₃)₂N). The formation of a bridge connection has the character of a „nucleophilic reaction under electrophilic conditions” in all cases. The structures of all compounds were established by NMR spectroscopy.

Some time ago, we reported on the preparation and constitution of 8,8'-methylthio-3-commo-3-cobalta-bis(1,2-dicarba-*closo*-dodecaborane(11)), 8,8'-CH₃S(C₂B₉H₁₀)₂.Co^{III} (*I*) (ref.¹). In another paper, we describe² a reasonable synthesis of this compound together with a series of its S-alkyl analogs and we compare properties of compound *I* with the 8,8'-CH₃S₂(C₂B₉H₁₀)₂Co(III) compound where there is —S—S— bridge.

The subject of this contribution is a description of a series of further compounds similar to compound *I*, in which a monoatomic bridge-connection is formed by oxygen, selenium, tellurium or nitrogen atoms, such as 8,8'-RO(C₂B₉H₁₀)₂Co(III) (*IIa, b*), 8,8'-CH₃Se(C₂B₉H₁₀)₂Co(III) (*III*), 8,8'-CH₃Te(C₂B₉H₁₀)₂Co(III) (*IV*) and 8,8'-R¹R²N(C₂B₉H₁₀)₂Co(III) (*Va-c*).

The structures of compounds *I-V* were determined by a combination of the mass spectra, ¹¹B and ¹H-NMR spectroscopy. The schematized ¹¹B NMR of representative derivatives of this series (Fig. 1) have the main features of the parent (1,2-C₂B₉H₁₁)₂Co⁽⁻⁾ anion³, modified by substitution in positions B₍₈₎ and B_(8'). According to the molecular mass, determined by high resolution mass spectrometry (Table I), the separate compounds contain only one RO (*II*), CH₃Se (*III*), CH₃Te (*IV*) or (CH₃)₂N (*Vc*) group which must be therefore bound simultaneously to atoms

TABLE I
Some Properties of Compounds *I–V* of the Formula $8,8'-X(C_2B_9H_{10})_2Co^{III}$

Compound X	m/e calc. ^a (found)	R_F	Absorption maxima ^b $\lambda(\epsilon)$
<i>Ia</i> CH ₃ O	356·2756 (356·2755)	0·27 ^c	255 (21 580), 292 (10 240) 408 (1 380), 510 (1 019)
<i>Ib</i> C ₂ H ₅ O	370 (370)	0·26 ^c	254 (20 825), 292 (10 090) 408 (1 320), 510 (981)
<i>III</i> CH ₃ Se	421·2010 (421·2011)	0·20 ^c 0·68 ^d	250 (vw, sh), 296 (27 190) 322 (vw, sh), 450 (505), 485 (515)
<i>IV</i> CH ₃ Te	470·1874 (470·1879)	0·20 ^c 0·68 ^d	249 (vw, sh), 305 (20 010), 321 (vw, sh), 473 (440)
<i>Va</i> H ₂ N	341·2759 (341·2756)	0·04 ^c 0·44 ^d	259 (31 580), 294 (vw, sh), 415 (1 400), 498 (1 020)
<i>Vb</i> CH ₃ NH	355 (355)	0·12 ^c 0·52 ^d	
<i>Vc</i> (CH ₃) ₂ N	369 (369)	0·30 ^c 0·61 ^d	259 (29 380), 293 (vw, sh), 413 (1 230), 498 (920)

^a ¹H, ¹¹B, ¹²C, ¹⁴N, ¹⁶O, ³²S, ⁵⁹Co, ⁸²Se, ¹³⁰Te were calculated with the particular compounds; ^b dichloromethane; ^c TLC on Silufol foil, benzene–hexane 1 : 2 as eluent; ^d TLC on Silufol foil, benzene as eluent.

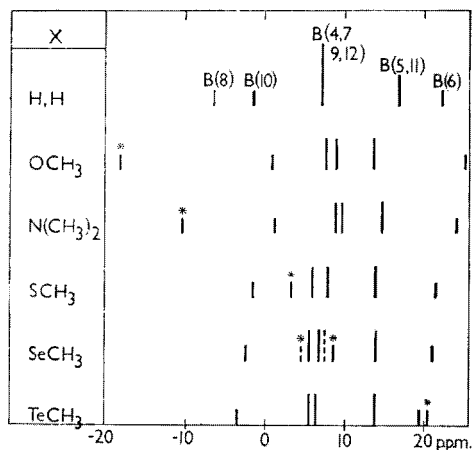


FIG. 1

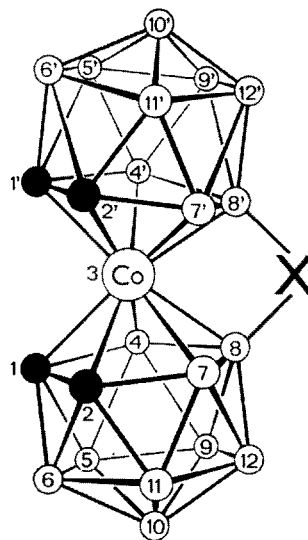
Correlation Diagram of ¹¹B-NMR Chemical Shifts of Particular Signals of the 8,8'- $X(C_2B_9H_{10})_2Co$ Compounds *I–V* (Ordered According to the Decreasing Sanderson's Electronegativity of the Bridging Atom) in Comparison with the Parent $(C_2B_9H_{11})_2Co^{(-)}$ Anion

* Singlet, — — — less probable position of the signal.

B₍₈₎ and B_(8') forming thus the monoatomic bridge between them. The resultant molecule has a character of a "zwitterion" in which the bridge atom represents the positive part and the whole cage skeleton the negative part of an overall neutral molecule.

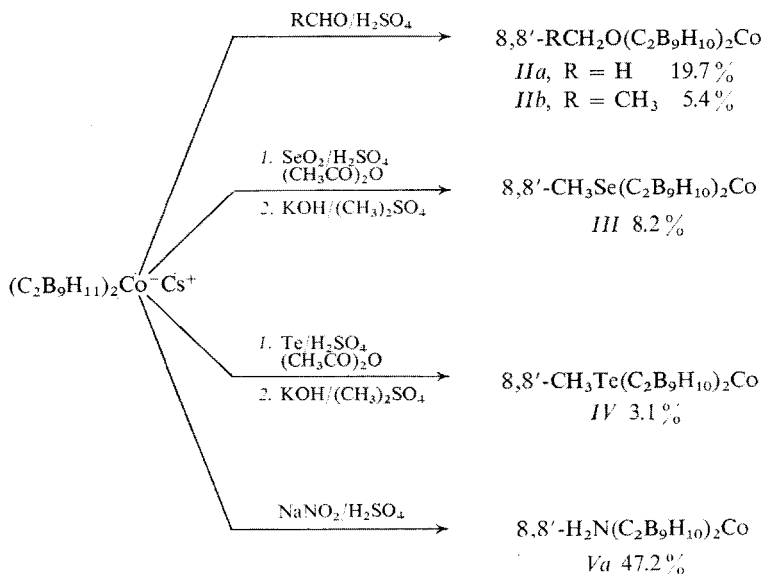
Recently, the basic structure of these compounds with the monoatomic bridge was confirmed⁴ by the X-ray diffraction analysis of the compound *I*a. This study proved our hypothesis¹ that both pentagonal planes facing to the Co atom are not parallel, but (due to the presence of a bridge with a short B—X bond, 1.50 Å)

○ BH
● CH



- I*, X = SCH₃
*I*a, X = OCH₃
*I*b, X = OC₂H₅
III, X = SeCH₃
IV, X = TeCH₃
*V*a, X = NH₂
*V*b, X = NHCH₃
*V*c, X = N(CH₃)₂

they form an angle of approx. 28° with one another. This method also showed that the methyl group does not lie in the plane bisecting the atoms O, B₍₈₎, B_(8'), Co but makes an angle of 149° with that plane.



Compounds *II–V* were prepared by specific reactions, the common characteristic of which is apparently a “nucleophilic substitution under electrophilic conditions”⁵: In the last reaction, two by-products are formed containing a two-atom —O—N— bridge; they will be discussed in another contribution. Alkylation of compound *Va* in heterogeneous medium proceeds only to the stage of the N-methyl derivative 8,8'-CH₃NH(C₂B₉H₁₀)₂Co(III) (*Vb*), in homogeneous medium the dimethyl derivative 8,8'-(CH₃)₂N(C₂B₉H₁₀)₂Co(III) (*Vc*) is formed. Interestingly, compounds *Va* and *Vb* do not behave as typical acids. They are not soluble even in 10% aqueous KOH and they do not form an insoluble potassium salt. The almost identical positions of absorption maxima in UV spectra with compounds *Va* and *Vc* (Table I) indicate the insignificant acidity of N—H bonds in compounds *Va* and *Vb*.

In the preparation of compound *Iib* it is not necessary to add acetaldehyde into the reaction mixture as it is formed *in situ* by reduction of a part of the acetic an-

TABLE II

100 MHz ¹H-NMR Spectra of the 8,8'-X(C₂B₉H₁₀)₂Co Compounds (p.p.m. relative to tetramethylsilane, solvent: C₆D₆)

Compound	X	δCH (rel. int.)	δCH ₃ (rel. int.)
<i>Iia</i>	CH ₃ O	3.74 (4)	3.96 (3)
<i>III</i>	CH ₃ Se	4.18 (4)	2.56 (3)
<i>IV</i>	CH ₃ Te	4.18 (4)	2.92 (3)
<i>Vc</i>	(CH ₃) ₂ N	3.83 (4)	2.77 (6)

TABLE III

Chemical Shifts of ¹¹B-NMR Signals at 70.6 MHz of the 8,8'-X(C₂B₉H₁₀)₂Co Compounds *I–V* and of the Parent (C₂B₉H₁₁)₂Co⁽⁻⁾ Anion (p.p.m. rel. to BF₃·O(C₂H₅)₂; solvent: CD₃COCD₃)

Compound	X	B(8) ^a	B(10)	B(4,7 + 9,12)	B(5,11)	B(6)
<i>Iia</i>	CH ₃ O	-18.2 ^b	1.1	7.8; 9.0	13.6	25.2
<i>Vc</i>	(CH ₃) ₂ N	-10.3 ^b	1.3	8.9; 9.7	14.8	24.1
<i>I</i>	CH ₃ S	3.4 ^b	-1.5	6.0; 7.9	14.0	21.5
<i>III</i>	CH ₃ Se	8.5 ^{b,c} (4.6) ^{b,c}	-2.2	5.6 ^c ; 6.9 (7.6) ^c	14.0	21.1
<i>IV</i>	CH ₃ Te	20.6 ^b	-3.3	5.6; 6.4	13.9	19.5
(C ₂ B ₉ H ₁₁) ₂ Co ⁽⁻⁾		-6.5	-1.5	7.1; 7.1	16.9	22.3

^a Substituted position; ^b singlet; ^c probable (less probable) position of signals shown by Peak Resolver in the overlapped areas.

hydride by a transfer of the hydride ion from position B₍₈₎ of a metallocarborane skeleton to the acetylum cation. This removal of the hydride anion from the most negative position of a heteroborane skeleton is the primary step with all "nucleophilic reductions under electrophilic conditions"⁵.

Compounds *II–V* are red, neutral, and can be easily checked by thin-layer chromatography on silica gel. Even though the *R_F* values of compounds *III*, *IV* and *I* (ref.²) are superposed, we can detect the presence of each compound in a mixture by comparing the character of the developing spots relative to the spots of the pure components. The substances *II–V* have no defined melting points and decompose above 300°C. Some properties of compounds *II–V* are shown in the Table I; the ¹H-NMR chemical shifts are in the Table II and ¹¹B-NMR chemical shifts are gathered in the Table III. Fig. 1 documents that the ¹¹B-NMR spectra of compounds *I–V*, ordered according to the decreasing Sanderson's electronegativity value of the substituent X, exhibit regularities in the changes of chemical shifts of the singlet ¹¹B signals, parallel to the changes found for the 8-X-1,2-C₂B₉H₁₀-3-Co(η-C₅H₅) series (X = F, Cl, Br, I)⁵.

EXPERIMENTAL

¹H-NMR spectra at 100 MHz and preliminary ¹¹B-NMR spectra at 32.1 MHz were measured on a Varian XL-100 instrument. The ¹¹B-NMR spectra at 70.6 MHz were measured on an instrument consisting of a pulsed NMR apparatus (built at Indiana University, Bloomington, U.S.A.), a Varian 51.7 kG superconducting magnet, and a 20K Nicolet 1080 series computer. UV and visible spectra were recorded on a Beckman DK 1, and IR spectra on a Beckman IR-20 A spectrometer. Mass spectra were measured on LKB 9000 and high resolution mass spectra were obtained on an AEI Model MS-902 mass spectrometer. The solvents used were of spectral grade for measurements and of chemical purity for preparative operations. Compounds *II–V* were purified by column chromatography on silica gel and eluted by a benzene-hexane 1 : 2 mixture or by pure benzene. The purity of single compounds was checked by thin-layer chromatography on Silufol (silica gel on aluminium foil, starch as binder, producer Kavalier, Votice, Czechoslovakia). The parent (C₂B₉H₁₁)₂Co⁽⁻⁾ Cs⁽⁺⁾ salt was prepared according to Hawthorne and coworkers⁶.

Compound *Ia*: To the solution of (C₂B₉H₁₁)₂Co⁽⁻⁾ Cs⁽⁺⁾ (2.3 g, 0.005 mol) and paraformaldehyde (1.0 g, 0.033 mol) in 10 ml of acetic anhydride, 1.5 ml of concentrated H₂SO₄ (1.5 ml, 0.028 mol) were added and the mixture was heated to 95°C for 2 h under nitrogen. The mixture was decomposed with water, the reaction product extracted into benzene and isolated by the column chromatography on silica gel; yield 0.35 g (19.7%) of *Ia*, red needles.

Compound *Ib*: The same procedure used for compound *Ia* was employed here however no acetaldehyde was added. The acetaldehyde needed was formed *in situ* by the reduction of acetic anhydride. 0.1 g (5.4%) of orange-red needles of compound *Ib* was isolated by chromatography.

Compound *III*: To the suspension of 1.4 g H₂SeO₃ (0.11 mol) in 60 ml of benzene, 8.0 g of acetic anhydride and 20 ml of concentrated H₂SO₄ were added. The selenous acid dissolved and the bottom-layer turned brown. After addition of 4.6 g (0.01 mol) of (C₂B₉H₁₁)₂Co⁽⁻⁾ Cs⁽⁺⁾, the mixture was shaken for 1 h at 20°C, refluxed for another 4 h and, at 10°C, decomposed with 30 ml water. Benzene as well as the aqueous layer were separated, the sticky orange inter-layer

was dissolved in 50 ml acetone and poured into the solution of 6.0 g KOH in 60 ml methanol. After an addition of 2 ml dimethyl sulphate the reaction mixture was shaken for 10 min. The excess of $(\text{CH}_3)_2\text{SO}_4$ was removed by shaking with 10 ml of 15% aqueous ammonia. Subsequently, 50 ml of benzene and 200 ml of water were added, the orange benzene layer was separated, washed with two 50 ml portions of water, filtered and concentrated to a volume of 10 ml. The resulting orange-red solution was carefully poured onto a column of 100 g of silica gel and the reaction products were eluted with benzene-hexane 1 : 2 mixture. The red layer of R_F 0.2 was mechanically separated, the product eluted with benzene, the solution concentrated to a volume of 10 ml and the remaining viscous liquid covered carefully with a layer of 30 ml hexane. After standing overnight, 0.35 g (8.2%) of red needles of compound *III* separated.

Compound IV: To the solution of 4.6 g (0.01 mol) of $(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}^{(-)}\text{Cs}^{(+)}$ in 20 ml of acetic anhydride, 3.4 g (0.025 mol) of powdered tellurium and 2 ml of concentrated H_2SO_4 were added. The mixture was heated for 4 h to 100°C, filtered, the main part of acetic anhydride was removed from the filtrate *in vacuo* of 10 Torr at a bath temperature of 80°C, the remainder was shaken in 50 ml of water and 50 ml of benzene. The water layer was separated, benzene was evaporated *in vacuo* from the combined benzene layer and orange-layer. The remainder was treated in the same manner as the inter-layer in the preceding experiment; 0.15 g (3.1%) of compound *IV* was obtained. When elementary tellurium was substituted by TeO_2 , the yield was so low that the presence of product *IV* was detectable only by TLC.

Compound Va: To the suspension of $(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}^{(-)}\text{Cs}^{(+)}$ (4.6 g, 0.01 mol) in 50 ml of benzene and 50 ml of concentrated H_2SO_4 , cooled to the semi-solid slurry stage, NaNO_2 (1.4 g, 0.02 mol) was added in one portion. The mixture was stirred for 1 h at +5°C, 3 h at room temperature and left to stand overnight. The red benzene layer was separated, poured onto a column of 200 ml of silica gel and eluted with benzene until the front reached the bottom of the column. The distinct layer at R_F 0.4 was removed mechanically, extracted with 200 ml of benzene, the extract concentrated to 50 ml, covered carefully with a layer of 200 ml hexane and left to stand overnight. Red needles of compound *Va* (1.6 g, 47.2%) separated. Two more by-products were present in the reaction mixture that were separated on the column as orange layers at $R_F = 0.06$ and 0.17 (benzene).

Monomethyl derivative Vb: To the solution of compound *Va* (0.35 g, 0.001 mol) in 20 ml of benzene were added 20 ml of aqueous KOH and 1.0 ml of dimethyl sulphate. After 20 min shaking, only a spot of the compound *Vb* was found by TLC in the reaction mixture. The benzene layer was separated, shaken with 10 ml of 15% aqueous ammonia for 5 min, washed with water and concentrated to a volume of 5 ml *in vacuo*. The remaining solution was then cautiously covered with 15 ml of hexane and left to stand overnight. Needles of compound *Vb* separated (0.3, 88.5%).

Dimethyl derivative Vc: A solution of compound *Va* (1.7 g, 0.005 mol) and dimethyl sulphate (3 ml, 0.032 mol) in 50 ml of benzene was added to the solution of 6 g KOH in 60 ml of ethanol. After 10 min shaking, the mixture exhibited only the presence of a new compound as shown by TLC (R_F 0.30, benzene-hexane 1 : 2). The mixture was decomposed with 10 ml of water and the benzene layer treated as in the preceding case. Compound *Vc* (1.6 g, 84.8%) was isolated in the form of red prism.

The mass spectra were measured by Dr V. Kubelka, the $^1\text{H-NMR}$ spectra at 100 MHz and B^{11} -at 32.1 MHz by Dr P. Trška of the Institute of Chemical Technology, Prague. The high resolution mass spectra were measured by Dr L. Dolejš, Institute of Organic Chemistry and Biochemistry, Prague. The UV and IR spectra were recorded by Drs F. Hanousek, F. Haruda and Mrs K. Procházková. All these colleagues are thanked for their assistance.

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