

**THE (e-1,7'-2,2')4,8'-8,4'-(BIS- $\mu$ -o-PHENYLENE)BISDICARBOLLIDO-COBALT(1-)ATE ION [3-Co-4,8'-8,4'(o-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>(-)</sup>.  
THE FIRST DOUBLY BRIDGED METALLACARBORANE COMPLEX.  
SYNTHESIS, PROPERTIES AND STRUCTURE**

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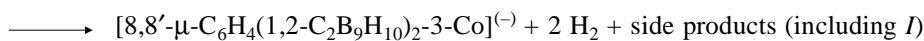
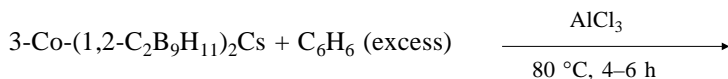
The first cobaltacarborane sandwich complex [3-Co-4,8'-8,4'(o-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>(-)</sup> with two o-phenylene bridges between both deltahedral ligands is described. Phenylene rings containing angle of 72° bind the Cs counter-ion probably via  $\pi$ -donation. This is why the solubility of Cs salt in water is extremely low. Synthesis, properties and structure of the Cs salt are described.

Synthesis, properties and structure of the unique cobaltacarborane ion (e-1,7'-2,2')4,8'-8,4'-(bis- $\mu$ -o-phenylene)bisdicarbollidocobalt(1-)ate (*I*) (Fig. 1) are described. It is apparently the first reported deltahedral sandwich complex with both ligands interconnected by a twofold external bridge.

The species, now recognized as *I* has been known in our laboratory for over 20 years as somewhat elusive side product of "direct arylenation" (Scheme 1) of the parent [3-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>(-)</sup> ion to the [8,8'- $\mu$ -C<sub>6</sub>H<sub>4</sub>(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>-3-Co]<sup>(-)</sup> ion<sup>1,2</sup> (*II*).

This unique "direct arylenation" is, however, very complicated in practice. First, the system is heterogeneous, and stirring, temperature, time and other factors are decisive for the final outcome. Second, the ratio of the cobaltacarborane cesium salt to aluminium chloride plays an important role as well. This is, why the yield of the orange side product *I* varies in a wide range.

Until recently the NMR spectra of this species were too complex to allow a proper assignment and to interpret them correctly. Knowing how difficult it was to connect



*II*

SCHEME 1

both deltahedral ligands by a single phenylene bridge (as in *II*) we did not suspect that the side product in question might contain two such bridges. Moreover, both vertices B(8,8') most prone to serve as bridgeheads were engaged already in the mono-bridged ion *II*.

The yellow parent cobaltacarborane ion changes to a deep red *II* on the introduction of one phenylene bridge. But the side product *I* is orange. We would have intuitively expected a further deepening of the red color on the introduction of the second phenylene bridge. All these factors contributed to our inability of recognizing the truth earlier.

Recent reinvestigation of the "direct arenylation" afforded the original "side product" *I* in approximately 40% yield. Its cesium salt is practically insoluble in water and in ethanol, but readily dissolves in acetone, acetonitrile and other polar solvents.

Its  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra, including the results of various "refining procedures" (e.g. the selective  $^1\text{H}$   $\{^{11}\text{B}\}$  decoupling, line narrowing,  $^{11}\text{B}$ - $^{11}\text{B}$  COSY 2D NMR, etc.) are gathered in the Table I. Two different C-H carborane signals of intensity 2 each and multiplets with intensities 2 : 2 : 4 of both phenylene rings are apparent in the  $^1\text{H}$  NMR spectrum. The  $^{11}\text{B}$  shows six signals of the intensity 1 and one signal of the intensity 3, this last being apparently due to a coincidental overlap of three signals of intensity 1; the two lowest field signals are singlets, belonging to two adjacent vertices, because the  $^{11}\text{B}$ - $^{11}\text{B}$  COSY 2D spectrum shows two distinct cross peaks between them. These facts

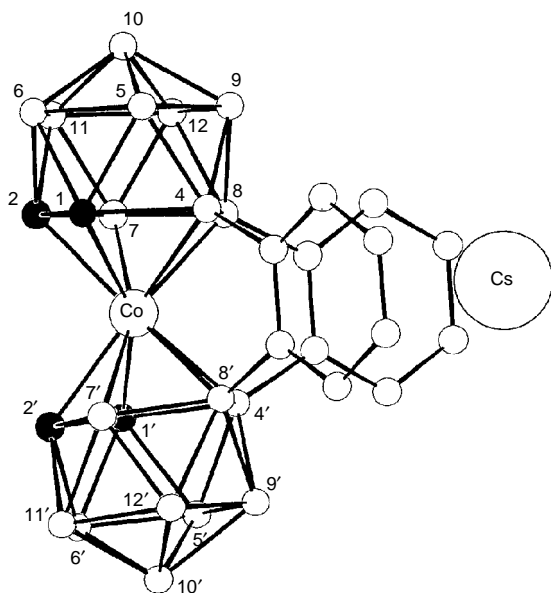


FIG. 1

Perspective view of one of the enantiomers of the anion  $[(e-1,7'-2,2')-p,p'-4,8'-8,4'-(\mu-\text{C}_6\text{H}_4)_2(1,2-\text{C}_2\text{B}_9\text{H}_9)_2-3-\text{Co}]^{(-)}$ ; terminal hydrogens are omitted for clarity.  $\circ = \text{B}$ ;  $\bullet = \text{C}$

indicate that there are two NMR equivalent icosahedral ligands externally bridged by two *o*-phenylene rings involving only B-vertices of the sandwich framework. The FAB mass spectrum of the Cs salt of *I* shows the *m/z* ratio 475 in agreement with the calculated value for  $^{12}\text{C}_{16}^{1}\text{H}_{26}^{11}\text{B}_{18}^{59}\text{Co} = [(\text{C}_6\text{H}_4)_2(\text{C}_2\text{B}_9\text{H}_9)_2\text{Co}]^{(-)}$ . This mass spectrum strongly supports the NMR results.

There exist three possibilities of connection of both  $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$  ligands by two phenylene bridges involving B-vertices 4,8'-8,4'. Only one possibility exists if both pentagonal ligand planes are arranged prismatically (Fig. 2a); with an antiprismatic arrangement we have to consider two possibilities (Fig. 2b, 2c). All three isomers would show the same general pattern of  $^1\text{H}$  and  $^{11}\text{B}$  NMR signals as has been actually found (Table I). The recent X-ray diffraction study<sup>3</sup> confirmed the possibility shown in Fig. 2a as corresponding to the species *I* (sketched in Fig. 1).

The phenylene ring planes in *I* are mutually inclined by  $72^\circ$  and would intersect in the original symmetry axis (defined by centers of both pentagons and crossing the central Co in the anion). This arrangement might favor a bonding of a suitable counterion, e.g.  $\text{Cs}^+$  or  $\text{Cl}_2\text{Al}^+$  between these rings due to a  $\pi$ -donation. And indeed, X-ray diffraction clearly shows the  $\text{Cs}^+$  cation "sandwiched" between both phenylene rings. We are not aware of any other case of a distinct  $\pi$ -coordination of an aromatic ring to an alkali metal ion.

In the alternative (still theoretical) antiprismatic isomers (Fig. 2b, 2c) both phenylene rings are spiralwise arranged akin to two adjacent blades of a five-blade Kaplan turbine. Such an arrangement practically excludes a formation of inner complexes via the  $\pi$ -donation. This subtle difference might be a reason why only type in Fig. 2a is obtained in a real experiment ( $\text{Cs}^+$  or  $\text{Cl}_2\text{Al}^+$  template effect?). However, the mechanism of the

TABLE I  
 $^1\text{H}$  and  $^{11}\text{B}$  NMR data ( $\delta$ , ppm; *J*, Hz) of the bisphenylene derivative *I* Cs salt

Position	$^{11}\text{B}$				$^1\text{H-B}$
	$\delta$	multiplicity	intensity	<i>J</i> (B,H), Hz	
8	23.41	s	1	—	—
4	12.68	s	1	—	—
10	-3.94	d	1	140	2.74
7, 9, 12	-6.18	(d)	3	?	2.24, 2.34, 2.58
5	-14.44	d	1	151	not observed
11	-18.76	d	1	149	1.73
6	-21.18	d	1	156	1.99

$^1\text{H-C}$  signals: 3.59, 2 H and 4.81, 2 H (carborane); 7.09 d, 2 H and 6.93 d, 2 H and 6.88 quin, 4 H (phenylene).

“direct arylenation” is still obscure. There are scores of experimental observations provoking speculations. Thus, neither  $\text{BCl}_3$  nor  $\text{FeCl}_3$  catalyze this reaction. In the presence of these reagents the benzene supernatant remains colorless, whereas with  $\text{AlCl}_3$  the yellow-orange parent cobaltacarborane ion enters almost instantaneously into benzene solution. But even with  $\text{AlCl}_3$  no hydrogen is evolved at ambient temperature, although a gradual formation of the red mono-bridged ion *II* takes place, whereas the doubly bridged ion *I* is apparently missing.

We believe that the primary intermediate of the “direct arylenation” is a pseudo-zwitterion  $[3\text{-Co-(1,2-C}_2\text{B}_9\text{H}_{11})_2]^{(-)} [\text{AlCl}_2]^{(+)}$  in which the  $\text{Cl}_2\text{Al}^+$  moiety is bound to the metallacarborane ion via the  $\text{B(8,8')-H}\dots\text{AlCl}_2$  bridges. The bridge hydrogen(s) might react with the  $\text{C}_6\text{H}_6 \cdot \text{AlCl}_3$  complex under the formation of  $\text{B(8)-C}_6\text{H}_7$  and/or  $\text{B(8,8')(\text{C}_6\text{H}_7)_2}$  intermediates. Disproportionation (at ambient temperature) or dehydrogenation at elevated temperature would offer the  $\text{B(8)-Ph}$  and/or  $\text{B(8,8')Ph}_2$  intermediates; an intramolecular cyclization of the former species would give rise to the mono-bridged ion *I*. An extensive research aimed at final elucidation of these puzzles continues.

### Comments to Nomenclature

The discoverer<sup>4</sup> of the parent  $[3\text{-Co-(1,2-C}_2\text{B}_9\text{H}_{11})_2]^{(-)}$  ion coined for it a semitrivial name – bis(1,2-dicarbollido)cobalt(1–)ate ion instead of the more correct but inconvenient 3,3'-*commo*-cobaltabis(1,2-dicarba-*closo*-dodecaborane)(1–)ate. Due to a free rotation of both icosahedral ligands around the symmetry axis several mutual conformations of both pentagonal ligand planes of the sandwich forming  $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$  ligands are possible; they eventually may become fixed, e.g. by external bridges. Considering

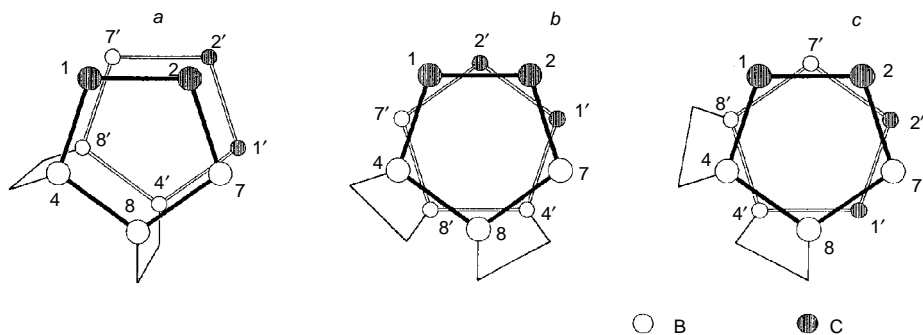


FIG. 2

Three possible conformations and bridge arrangements in the species *I*: *a* (e-1,7'-2,2')-p,p'-; *b* (s-1,2'-2,1')-p,p'-; *c* (s-1,7'-2,2')-p,p'- (For clarity, only both pentagonal ligand planes are sketched (Co being sandwiched between them); both phenylene rings are schematically indicated. Only one enantiomer of each isomer is shown in this scheme.)

this possibility we have suggested to designate such distinct conformations by nomenclature means, e.g. as (s-1,x'-2,y')(s = staggered = antiprismatic) or (e-1,x'-2,y') (e = eclipsed = prismatic), etc.<sup>5</sup>. A further complication arises due to the asymmetry of this species and the consequent prochirality. Fortunately, many years ago in a similar situation<sup>6</sup> we suggested to solve this problem marking the direction of deployment of the numbering spirals, applied in the respective case, by pictograms  $\sigma$  (clockwise) and  $\rho$  (anticlockwise). Thus, any enantiomer can be unambiguously described. For a proper description of the new bis-bridged species a merger of these nomenclature principles seems to be necessary in order to keep the names manageable. So we suggest to apply the combination of the semitrivial nomenclature for the parent sandwich<sup>1</sup> with our conformation descriptors<sup>5</sup> and the enantiomer designation<sup>6</sup> throughout this article.

## EXPERIMENTAL

### Apparatus and Chemicals

The NMR spectra were measured in deuteroacetone using a Varian UNITY 200 and 500 spectrometer at 64.2 and 160.36 MHz for <sup>11</sup>B, and 200.0 and 500 MHz for <sup>1</sup>H nuclei. The FAB mass spectrum was recorded on a Mass Spectrometer ZAB-EQ, VG Analytical, X-ray diffraction was carried out on a CAD4, Enraf-Nonius and UV-VIS spectra [ $\lambda_{\max}$ , nm ( $\epsilon_{\max}$ )] were measured using Hewlett-Packard 8452A diode-array spectrometer ( $l = 1$  mm cuvette) and acetonitrile as the solvent.

All reagents and solvents were of analytical grade and were used without further treatments. Experiments were carried out under dry nitrogen unless stated otherwise.

### Synthesis and Separation of *I* and *II*

The procedure is a slightly modified "direct arylenation" originally<sup>2</sup> aimed at the anion *II*.

A finely divided mixture of the [3-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>(-)</sup> Cs<sup>+</sup> salt (4.6 g, 10 mmol) and AlCl<sub>3</sub> (4.0 g, 30 mmol) in benzene (60 ml) was stirred for 6 h at ambient temperature and additional 4 h at 80 °C; 20 mmol of H<sub>2</sub> evolved during the heating step. After cooling to the ambient temperature, the red solids (fraction A) were sucked off from the red-brown benzene solution and rinsed with benzene (15 ml). The insoluble fraction A contained almost pure Cs salt of *I*, whereas the red ion *II* remained dissolved in benzene (fraction B). The solids A were treated with 75% ethanol (50 ml) with external cooling by tap water, and dissolved by addition of acetone until a clear orange-red solution was obtained. Acetone was evaporated at 80 °C and brick-red crystals of *I* Cs salt precipitated (2.18 g, 36%, TLC pure product,  $R_F$  0.41 in acetonitrile-chloroform 1 : 2). Some of *II* remained in the mother liquors.

The ion *II* was isolated from the benzene filtrate (fraction B); upon addition of 10% hydrochloric acid (50 ml) the red precipitate of the conjugate acid of *II* separated, whereas a mixture of various orange anions remained in the benzene supernatant. The red precipitate was sucked off, rinsed twice with benzene (10 ml), dissolved in acetone and the deep red solution was added to CsCl (1.5 g) in water (50 ml). After evaporation of acetone in vacuo, the red Cs salt of *II* was sucked off and recrystallized from 40% ethanol; 2.30 g (44%) of a TLC pure product ( $R_F$  0.37 in acetonitrile-chloroform 1 : 2).

UV spectrum,  $\lambda_{\max}$  ( $\epsilon_{\max}$ ): 207 (290), 273 (12), 288 (10). Crystals of I-Cs salt for X-ray diffraction<sup>3</sup> were grown from a solution of the above I-Cs salt in ethanol (30 ml), water (20 ml) and

acetone (10 ml) by a slow evaporation at ambient temperature; brilliant orange-red prisms were obtained. The X-ray study shall be published soon elsewhere.

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## REFERENCES

1. Plesek J., Hermanek S.: Czech. 188 587 (15 .7. 1981); Chem. Abstr. 96, 143085 (1982).
2. Plesek J., Hermanek S.: Collect. Czech. Chem. Commun. 43, 1325 (1978).
3. Cisarova I.: Private communication.
4. Hawthorne M. F., Young D. C., Andrews T. D., Howe T. D., Pilling R. L., Pitts A. D., Reintjes M., Warren L. F., jr., Wegner P. A.: J. Am. Chem. Soc. 90, 879 (1968).
5. Janousek Z., Plesek J., Hermanek S., Base K., Todd L. J., Wright W. F.: Collect. Czech. Chem. Commun. 46, 2818 (1981).
5. Plesek J., Hermanek S., Stibr B.: Collect. Czech. Chem. Commun. 34, 3233 (1969).