CHEMISTRY OF COBALT BIS(DICARBOLLIDES). A REVIEW

Igor B. SIVAEV* and Vladimir I. BREGADZE

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science,
28 Vavilov Str., 117813, Moscow, Russia; e-mail: bre@ineos.ac.ru

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We have the pleasure to dedicate this article to Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his outstanding contribution to cage-boron chemistry.

Synthesis and chemical properties of cobalt bis(dicarbollides) [*commo*-3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ and [*commo*-2,2′-Co(1,7-$C_2B_9H_{11})_2]^-$ and their derivatives are reviewed. An attention is also paid to potential applications of cobalt bis(dicarbollides). A review with 132 references.

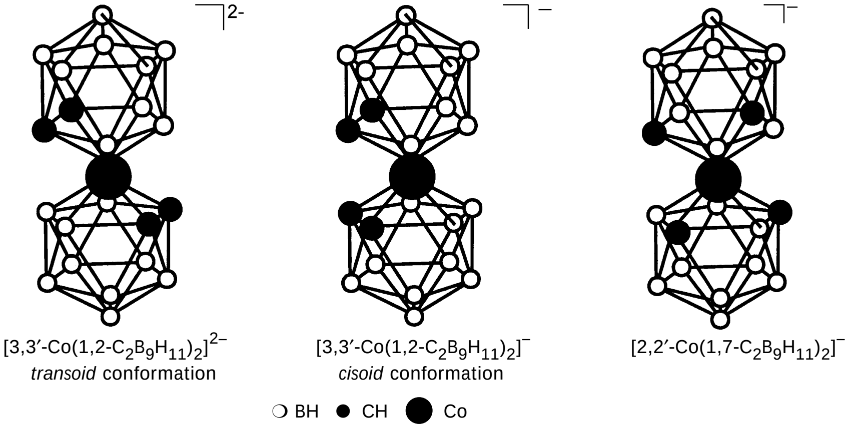
Key words: Boranes; Carboranes; Cobalt; Sandwich complexes; Metallacarboranes.

1. COBALT BIS(DICARBOLLIDE) ANIONS

The synthesis of the first metallacarboranes was reported in 1965 (refs[1,2]). The 18-electron low-spin d^6 cobalt bis(1,2- and 1,7-dicarbollides) [*commo*-3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ (**1**) and [*commo*-2,2′-Co(1,7-$C_2B_9H_{11})_2]^-$ (**2**) were among the very first metallacarboranes synthesized. At present their chemistry is one of the most elaborated in the metallaborane chemistry.

The classical approach to the synthesis of the [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ anion (Fig. 1) consists in the partial degradation of *ortho*-carborane with base into *nido*-[7,8-$C_2B_9H_{12}]^-$ followed by its deprotonation to the [7,8-$C_2B_9H_{11}]^{2-}$ dianion and reaction with $CoCl_2$. Usually the dicarbollide dianion is generated *in situ* by the treatment of *nido*-[7,8-$C_2B_9H_{12}]^-$ with sodium hydroxide in aqueous solution[3,4] (78% yield as the cesium salt and 74% yield as the potassium salt), with sodium hydride in tetrahydrofuran[2,3] (72% yield as the cesium salt), or with potassium *tert*-butoxide in 1,2-dimethoxyethane[5] (95% yield as the cesium salt). The same approach was used for synthesis of various derivatives of the cobalt bis(1,2-dicarbollide) (see below). In some cases the deprotonation with n-butyllithium in tetrahydrofuran was used[6]. The synthesis of **1** under mechanical activation of the solid reagents in a vibrating ball mill was also reported[7]. The electrolysis of the K[7,8-$C_2B_9H_{12}$] solution in dimethyl sulfoxide on the cobalt anode yields up to 54% of **1** isolated as the potassium salt[8].

Crystal structure of Cs[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] was determined[9] in 1967; however, positions of the carbon atoms were not determined and hence the ligand orientation was not established. Later, the crystal and molecular structure of (Et_3NH)[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] was determined[10]. The [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion consists of two $(C_2B_9H_{11})^{2-}$ (dicarbollide) units sandwiched around a formal Co^{3+} ion with the C_2B_9 faces on the two ligands nearly parallel (dihedral angle 3.7°). The vector distances from cobalt to the C_2B_9 planes are virtually identical (1.466 and 1.476 Å), and the metal is approximately equidistant from the facial boron and carbon atoms although the Co–C distances are slightly shorter that the Co–B vectors (mean values 2.046(2) and 2.097(2) Å, respectively). The two $(C_2B_9H_{11})^{2-}$ ligands are mutually rotated by 37°. This produces a staggered orientation of the carborane cages with the two C–C edges in close proximity, the molecule having approximate overall C_2 symmetry.



[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^{2-}$
transoid conformation

[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$
cisoid conformation

[2,2′-Co(1,7-$C_2B_9H_{11}$)$_2$]$^-$

FIG. 1
Structure of cobalt bis(dicarbollide) anions

The $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion has been characterized by the methods of UV (refs[3,11]), IR (refs[3,12]), Raman (refs[12–14]), NMR (refs[15,16]), X-ray photoelectron[17], and X-ray[18] spectroscopy. Diamagnetic susceptibility of $Cs[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ was determined[19,20]. Electrochemical behaviour of the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion in various solvents (acetone, acetonitrile, 1,2-dimethoxyethane, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, butano-4-lactone, propylene carbonate) was investigated[3,5,21–26]. Two stepwise reversible one-electron reduction transitions and a one-electron oxidation transition were revealed.

Reduction of **1** with 1 equivalent of sodium amalgam or cesium metal in 1,2-dimethoxyethane (DME) forms the brown cobalt(II) dianion $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^{2-}$ (**3**), which reverts back to yellow-orange **1** upon action of 0.5 equivalent of iodine in tetrahydrofuran[27]. Compound **3** is paramagnetic 19-electron complex. The molecular structure of $[Cs(DME)_4]_2[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ shows the carbon atoms occuping *transoid* rotational geometry about the cobalt center, consistent with the structure of isoelectronic nickel(III) bis(dicarbollide)[28]. The dianion **3** has approximate C_{2h} molecular symmetry. Addition of water to the deprotonated material causes reversion to the parent anion[27].

Refluxing **1** with 30% aqueous alkali results in the removal of one of the BH-vertices adjacent to the C–C edge forming the *nido*-$[3,9'\text{-Co}(1,2\text{-}C_2B_9H_{11})(7',8'\text{-}C_2B_8H_{11})]^{2-}$ complex anion which gives *closo*-$[3,1'\text{-Co}(1,2\text{-}C_2B_9H_{11})(2',4'\text{-}C_2B_8H_{10})]^-$ on oxidation with hydrogen peroxide[29,30]. Reaction of **1** with $CoCl_2$ in 30% refluxing aqueous alkali results in the multinuclear cobaltacarbaboranes of the (3,6)-1,2-dicarbacanastide family $[(C_2B_9H_{11})Co(C_2B_8H_{10})Co(C_2B_9H_{11})]^{2-}$ and $[(C_2B_9H_{11})Co(C_2B_8H_{10})Co(C_2B_8H_{10})Co(C_2B_9H_{11})]^{3-}$ (refs[21,31]).

Treatment of **1** with 1 equivalent of n-butyllithium in tetrahydrofuran results not in reduction, but in monodeprotonation with formation of purple $[1\text{-Li-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$. The doubly deprotonated blue species $[1,1'\text{-}Li_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ is formed in the reaction with 2 equivalents of n-butyllithium[27].

At present, a number of salts of the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion with various metal (Li^+, Na^+, K^+, Cs^+ (ref.[32]), Mg^{2+}, Ca^{2+}, Sr^{2+}, La^{3+}, Cu^+, Ag^+ (refs[16,33]), alkylammonium (Me_4N^+, Me_3NH^+, Et_4N^+, Et_3NH^+ (ref.[34]), $Me_3CNH_3^+$, Bu_4N^+, dodecyl(trimethyl)ammonium, $Me_2(Ph)NH^+$ (ref.[35]), piperidinium, pyridinium, methenammonium, ethylene-1,2-diammonium, tris(2-hydroxyethyl)ammonium) cations, triphenylmethylium[33], and hydrazinium cations, as well as with protonated amino acids (L-arginine, L-ornithine, L-lysine, glycine, L-valine, L-leucine, L-phenylalanine, L-tryptophane), glucosamine, cinchonine, and amides (dimethylformamide, dimethylacetamide, caprolactam) were prepared[16]. Thermal stability of the cesium[36,37], trimethylammonium[36–38], tetramethylammonium[36–39], tetraethylammonium[36,38], and pyridinium[36] salts was studied.

At present, synthesis of various salts and adducts of **1** was described: $[Zn(en)_2][3,3'-Co(1,2-C_2B_9H_{11})_2]_2$ (ref.[16]), $[Co(NH_3)_6][3,3'-Co(1,2-C_2B_9H_{11})_2]_3$ (ref.[22]), $Na[3,3'-Co(1,2-C_2B_9H_{11})_2]\cdot$2 Bipy (ref.[40]), $Na[3,3'-Co(1,2-C_2B_9H_{11})_2]\cdot$2 Phen (ref.[40]), $Co[3,3'-Co(1,2-C_2B_9H_{11})_2]\cdot$4 Bipy (ref.[40]), $Co[3,3'-Co(1,2-C_2B_9H_{11})_2]\cdot$4 Phen (ref.[40]), $[(\eta^5-C_5H_5)_2Fe][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (refs[41–43]), [(ethylene-bis(η^5-4,5,6,7-tetrahydroinden-1-yl)M(H) $(PhNMe_2)][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (M = Zr, Hf) (ref.[44]), $[(\eta^5-C_5H_5)_2ZrMe][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[35]), $[(\eta^5-C_5Me_5)_2ThMe][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[34]), $[(\eta^5-C_5Me_5)_2-ThCH_2SiMe_3][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[34]), $[(\eta^5-C_5Me_5)_2Th(H)][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[34]), $[Ir(CO)(PPh_3)_3][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[33]), $[(\eta^5-C_5H_5)-Fe(\eta^6-1,4-xylene)][3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[33]), $[Mo_3(\mu_3-S)(\mu_2-S_2)_3(Et_2NCS_2)_3]-[3,3'-Co(1,2-C_2B_9H_{11})_2]$ (ref.[45]). The $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ anion is one of the least coordinating anions. The ligand field strength of a series of weakly binding anions for Fe(III) was estimated from S = 3/2,5/2 spin state mixing in iron(III) porphyrins Fe X(TPP) (TPP = 5,10,15,20-tetraphenyl-21*H*,23*H*-porfine) and was found[46] to increase in the series $[1-CB_{11}H_{12}]^- < SbF_6^- < [3,3'-Co(1,2-C_2B_9H_{11})_2]^- < AsF_6^- < ClO_4^- < BF_4^- < I^- < Br^- < Cl^-$.

Toxicity and pharmacokinetics of $K[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ in tumor-bearing rats were studied[47,48]. The LD_{50} value was found to be 0.0875 mg/kg. Toxicity of $H[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ and its mutagenicity to *Salmonella typhimurium* and *Drosophila melanogaster* were determined[49].

Chemistry of cobalt bis(1,7-dicarbollide) was studied in a less extent. The $[2,2'-Co(1,7-C_2B_9H_{11})_2]^-$ anion (Fig. 1) can be prepared by partial degradation of *meta*-carborane to the *nido*-$[7,9-C_2B_9H_{12}]^-$ followed by its deprotonation with sodium hydroxide in aqueous solution or with sodium hydride in tetrahydrofuran and reaction of the $[7,9-C_2B_9H_{11}]^{2-}$ dianion formed with $CoCl_2$ (90 and 80% yield as cesium salt for the aqueous and non-aqueous method, respectively)[3].

The $[2,2'-Co(1,7-C_2B_9H_{11})_2]^-$ anion has been characterized by the methods of UV, IR, and NMR spectroscopy[3]. Electrochemical behaviour of the $[2,2'-Co(1,7-C_2B_9H_{11})_2]^-$ anion in acetone was investigated using the cyclic voltammetry method[3], reversible one-electron reduction at –1.17 V (*vs* SCE) being revealed. Thermal stability of the cesium, trimethylammonium, tetramethylammonium, and tetraethylammonium salts of the $[2,2'-Co(1,7-C_2B_9H_{11})_2]^-$ anion was studied[38].

2. DERIVATIVES OF $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$

2.1. Carbon Substituted Derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$

A general approach to synthesis of C-substituted derivatives of cobalt bis(1,2-dicarbollide) consists in preparation of the corresponding substituted *ortho*-carboranes, their degradation into the *nido*-7,8-dicarbaundecaborates, followed by deprotonation and reaction with cobalt(II) chloride. A mixture of two geometric isomers (racemic mixture and *meso* form) arises from initial carboranes bearing non-identical substituents (Table I). The attempt to prepare $[1,1',2,2'\text{-Ph}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ by this way was not successful[54].

The same approach was used by Hawthorne *et al.*[55] to synthesize cobaltcarboranes containing C-bridged dicarbollide ligands (Fig. 2). Compounds with tri-, tetra-, and pentamethylene-bridged carbon-linked dicarbollide ligands were prepared $[1,1'\text{-}\mu\text{-}\{(\text{CH}_2)_n\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (n = 3 (**23**), 46%; n = 4 (**24**), 61%; n = 5 (**25**), 20%). In each instance, *meso* and racemic forms were obtained from the reaction of the diastereomeric-bridged carborane precursors and cobalt(II) chloride. Compounds $(\text{Ph}_3\text{MeP})[1,1'\text{-}\mu\text{-}\{(\text{CH}_2)_3\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\cdot 1/2\ \text{CH}_2\text{Cl}_2$ and $(\text{Ph}_3\text{MeP})[1,1'\text{-}\mu\text{-}\{(\text{CH}_2)_4\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ have been characterized by single-crystal X-ray diffraction. The C_2B_9 faces in both the structures are noticeably non-parallel (the angles between normals to the two bonding planes are 7(2) and 9(2)° for **23** and **24**, respectively).

X =	
$(\text{CH}_2)_3$	**23**
$(\text{CH}_2)_4$	**24**
$(\text{CH}_2)_5$	**25**
$(\text{CH}_2)_2\text{N(Ts)}(\text{CH}_2)_2$	**26**
CH_2OCH_2	**27**
CH_2SCH_2	**28**
$\text{CH}_2\text{SO}_2\text{CH}_2$	**29**
$\text{SCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{S}$	**30**

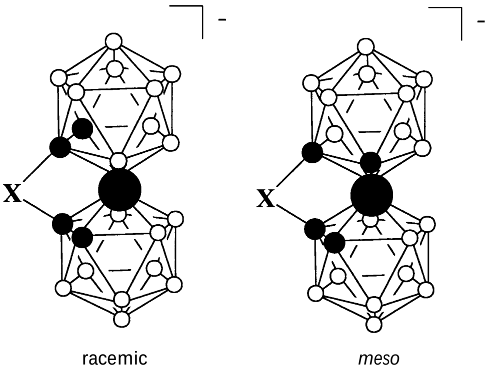


FIG. 2
C,C′-bridged cobalt bis(1,2-dicarbollide) derivatives

TABLE I

Carbon substituted derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ prepared from the corresponding *ortho*-carboranes

Compound	Yield, %	Ref.
$[1,1',2,2'\text{-Me}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**4**)	63	3
$[1,1',2,2'\text{-Et}_4 3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**5**)	28	5
$[1,1',2,2'\text{-Et}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**5**)	91	5
$[1,2{:}1',2'\text{-di-}\mu\text{-}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**6**)	46	6
$[1,2{:}1',2'\text{-di-}\mu\text{-}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**6**)	75	6
$[1,2{:}1'2'\text{-di-}\mu\text{-}(\text{CH=CH–CH=CH})_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**7**)	50	50
$[1,1'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**8**)[a]	93	5
$[1,1'\text{-Ph}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**9**)[a]	70	3
$[1,1'\text{-Ph}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**9**)[a]	80	5
$[1,1'\text{-}\{\text{EtO}(\text{CH}_2)_3\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**10**)[a]	90	51
$[1,1'\text{-}\{\text{MeO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**11**)[a]	77	51
$[1,1'\text{-}\{\text{BuO}(\text{CH}_2)_3\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**12**)[a]	89	51
$[1,1'\text{-}(\text{MeOCH}_2\text{CH}_2)_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**13)**[a]	40	5
$[1,1'\text{-}(\text{MeOCH}_2\text{CH}_2)_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**13)**[a]	86	5
$[1,1'\text{-Bu}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**14**)[a]		52
$[1,1'\text{-}\{\text{MeO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**15**)[a]		52
$[1,1'\text{-}\{\text{BuO}(\text{CH}_2)_6\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ **(16)**[a]		52
$[1,1'\text{-}\{\text{Me}_2\text{CHCH}_2\text{O}(\text{CH}_2)_3\}_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**17**)[a]		52
$[1,1'\text{-}(\text{EtS})_2\text{-}3,3'\text{-Co}(1,2\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**18**)[a]	68	5
$[1,1'\text{-}(\text{EtS})_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**19**)[a]	35	5
$[1,1'\text{-}(\text{EtS})_2\text{-}2,2'\text{-Me}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**19**)[a]	79	5
$[1,1'\text{-}(\text{EtS})_2\text{-}2,2'\text{-Ph}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**20**)[a]	56	53
$[1,1'\text{-}(\text{MeS})_2\text{-}2,2'\text{-Ph}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**21**)[a]	51	53
$[1,1'\text{-}(\text{BuS})_2\text{-}2,2'\text{-Ph}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ (**22**)[a]	46	53

[a] Mixture of *meso* and racemic forms.

Aza-, oxa-, and thiaalkane-1,n-diyl-bridged carbon-linked cobalt bis(dicarbollides) $[1,1'\text{-}\mu\text{-}\{TsN(CH_2CH_2)_2\}\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**26**)[55] (61%), $[1,1'\text{-}\mu\text{-}(CH_2OCH_2)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**27**)[56] (65%), $[1,1'\text{-}\mu\text{-}(CH_2SCH_2)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**28**)[57] (44%) were prepared in the same manner. *Meso* and racemic forms of **26** were separated by HPLC techniques. The crystal structures of $(Ph_3MeP)[(\pm)\text{-}1,1'\text{-}\mu\text{-}(CH_2OCH_2)\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{10})_2]\cdot 1/2\ CCl_4$ (ref.[56]) and $(Ph_3MeP)[\textit{meso}\text{-}1,1'\text{-}\mu\text{-}(CH_2SCH_2)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[57]) were determined by X-ray diffraction. The angles between normals to the C_2B_9 faces are 6.4 and 8.1° for **27** and **28**, respectively. Oxidation of the cobalt bis(dicarbollide) thioether **28** with 3-chloroperoxybenzoic acid in methylene chloride results in the production of the corresponding sulfone $[1,1'\text{-}\mu\text{-}(CH_2SO_2CH_2)\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{10})_2]^-$ (**29**)[57]. The long-bridge cobalt bis(1,2-dicarbollide) $[1,1'\text{-}\mu\text{-}\{SCH_2CH_2(OCH_2CH_2)_3S\}\text{-}2,2'\text{-}Me_2\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_9)_2]^-$ (**30**) was prepared by similar way and its salts with macrocycle-complexed sodium or potassium cations were characterized by X-ray diffraction[58].

Another approach to synthesis of C-substituted derivatives of cobalt bis(dicarbollide) consists in its treatment with n-butyllithium followed by the reaction with alkyl halides[27]. Using 1 equivalent of n-butyllithium, monosubstituted C-alkyl derivatives $[1\text{-}R\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (R = CH_3 (**31**), n-C_6H_{13} (**32**)) were prepared, whereas the disubstituted derivatives $[1,1'\text{-}R_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (R = CH_3 (**8**), n-C_6H_{13} (**33**), $CH_2OCH_2CH_2OCH_3$ (**34**)) were obtained using 2 equivalents of n-butyllithium. In the case of methyl and hexyl derivatives, a mixture of *meso* and racemic forms was obtained, but for $[1,1'\text{-}(CH_3OCH_2CH_2OCH_2)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ the ±-isomers are formed selectively in the reaction. Treatment of **31** with n-butyllithium and methyl iodide gives $[1,2\text{-}Me_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)(1',2'\text{-}C_2B_9H_{11})]^-$ (**35**) (30%) as well as the mixture of *meso* and racemic forms of **8**. The attempts to alkylate dihalogeno derivatives $[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ failed[27].

The crystal structures of $(Ph_3MeP)[1,1',2,2'\text{-}Et_4\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]$ (ref.[5]), $Na[1,1'\text{-}Ph_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]\cdot 0.4\ C_6H_5CH_3$ (ref.[54]), and $Cs[1,1'\text{-}(CH_3OCH_2CH_2OCH_2)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[27]) were determined.

Mono- and dicarboxylic acids $[1\text{-}HOOC\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (**36**) and $[1,1'\text{-}(HOOC)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**37**) were prepared by the treatment of the mono- and dilithium derivatives with carbon dioxide. The corresponding acyl chlorides were prepared[59] by the reaction with $SOCl_2$.

2.2. Boron Substituted Derivatives of $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$

Substitution at boron atoms of the $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ anion is much more studied than substitution at carbon atoms. As a rule, substitution proceeds at the boron atoms with maximum electron density.

The halogenation of **1** by gaseous chlorine in ethanol–tetrachloromethane or nitrobenzene–tetrachloromethane mixture proceeds alternatively in both dicarbollide ligands yielding successively 8- (**38**), 8,8′- (**39**), 8,8′,9- (**40**), 8,8′,9,9′- (**41**), 8,8′,9,9′,12- (**42**), and 8,8′,9,9′,12,12′- (**43**) chloro derivatives[60]. Complete resolution of mixtures of the derivatives containing 1–6 atoms of chlorine is possible by isotachophoresis[61,62]. The reaction of **1** with gaseous chlorine in a tetrahydrofuran–isopropanol solution in the presence of iron powder produces **39** (ref.[63]). The reaction of **1** with acidified aqueous sodium hypochlorite (HCl/NaOCl) results in the dichloro derivative **39** (ref.[63]). The reaction of **1** with *N*-chlorosuccinimide in refluxing tetrahydrofuran also gives **39**. γ-Irradiation of solution of **1** in a chloroform–benzene mixture gives **38**, whereas the γ-radiation-induced chlorination in the tetrachloromethane–nitrobenzene mixture results in formation of **38**, **39** or **43** depending on the dose absorbed[60].

$[9,9'-Cl_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**44**) and $[9,9',12,12'-Cl_4-3,3'-Co(1,2-C_2B_9H_9)_2]^-$ (**45**) were prepared by a general synthesis from $CoCl_2$ and the appropriate chloro-*ortho*-carboranes[60].

The reaction of **1** with bromine in methanol at ambient temperature results in $[8-Br-3,3'-Co(1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]^-$ (**46**) or $[8,8'-Br_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**47**) depending on the ratio of the initial reagents[60,64]. The reaction of bromine with **1** in a refluxing tetrahydrofuran solution gives dibromo derivative **47** (ref.[63]). Treatment of **1** with an excess of bromine in glacial acetic acid solution at the reflux temperature produces the hexabromo derivative $[8,8',9,9',12,12'-Br_6-3,3'-Co(1,2-C_2B_9H_8)_2]^-$ (**48**)[3,32]. The reaction of **1** with *N*-bromosuccinimide in refluxing tetrahydrofuran gives the dibromo derivative **47** (ref.[63]). Radiolysis of **1** in a nitrobenzene–tribromomethane mixture results in the stepwise formation of **46** and **47** (refs[64,65]). These derivatives were also obtained by the γ-irradiation of solution of **1** in a tribromomethane–methanol mixture[60]. $[9,9'-Br_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**49**) and $[9,9',12,12'-Br_4-3,3'-Co(1,2-C_2B_9H_9)_2]^-$ (**50**) were prepared by a general synthesis from $CoCl_2$ and the appropriate bromo-*ortho*-carboranes[6]. Preparation of silver and triphenylmethylium salts of the hexabromo derivative was described[33].

The reaction of **1** with iodine in methanol gives $[8-I-3,3'-Co(1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]^-$ (**51**) or $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**52**) depending on the initial reagent ratio[60]. Treatment of **1** with iodine in benzene at 80 °C in the presence of $AlCl_3$ gives the hexaiodo derivative $[8,8',9,9',12,12'\text{-}I_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$ (**53**)[60]. The reaction of **1** with iodine monochloride in refluxing methylene chloride affords the hexaiodo derivative **53** (ref.[67]).

The chemical stability of 8,8′- and 8,8′,9,9′,12,12′-halogeno derivatives of the cobalt bis(1,2-dicarbollide) rises very sharply in comparison with the parent cobalt bis(1,2-dicarbollide). The conjugated acids of the hexachloro and hexabromo derivatives withstand contact with 10 M HNO_3 without any change for many weeks, whereas the unsubstituted conjugated acid decomposes in contact with 5 M HNO_3 in a short time[16,68]. The 8,8′-dihalogeno derivatives are unchanged when refluxed in a tetrahydrofuran solution of $NaNH_2$ or when treated with a toluene solution of butyllithium at room temperature. The kinetic stability of this boron–halogen bond allows these compounds to withstand 3 M HNO_3 for periods in excess of 1 month[63].

The structures of the halogeno substituted cobalt bis(1,2-dicarbollides) $Cs[8\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (ref.[69]), $K[8,8'\text{-}Cl_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[70]), $(PPN)[8,8'\text{-}Cl_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[63]), $Cs[8,8'\text{-}I_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[71]), $(Me_4N)[8,8',9,9',12,12'\text{-}Br_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]$ (ref.[72]), and $Cs[8,8',9,9',12,12'\text{-}Br_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]$ (ref.[73]) were determined by X-ray diffraction. The dicarbollide ligands in the studied di- and hexahalogeno substituted cobalt bis(1,2-dicarbollides) have *transoid* conformation.

The complex $[8,8'\text{-}\mu\text{-}I\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (**54**) (Fig. 3) with a iodonium bridge between the dicarbollide ligands was prepared by heating **51** in benzene at 80 °C in the presence of $AlCl_3$. The complex **54** behaves as

X =				
	I	**54**	SCH_2CH_2CN	**82**
	OMe	**66**	SCH_2OCH_3	**83**
	OEt	**67**	SPh	**84**
	SMe	**74**	SeMe	**96**
	SEt	**75**	TeMe	**97**
	SBu	**76**	NH_2	**98**
	$SCH_2C_6H_5$	**77**	NHMe	**101**
	$SCH_2CH{=}CH_2$	**78**	NMe_2	**102**
	$SCH_2C{\equiv}CH$	**79**	$NHCH_2COOCH_3$	**104**
	SCH_2COOCH_3	**80**	PMe_2	**113**
	SH	**81**		

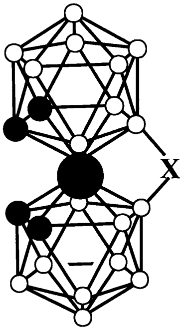


FIG. 3
8,8′-Single-atom-bridged cobalt bis(1,2-dicarbollide) derivatives

a Lewis acid to form with Lewis bases a family of uncharged derivatives [8-I-8′-L-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (L = SMe_2 (**55**), 1,4-dioxane (**56**), NH_3 (**57**), NMe_3 (**58**), Py (**59**))[74,75]. The ring-opening reaction of the dioxonium derivative **56** with $C_5H_{11}ONa$ in benzene at 60 °C gives [8-($C_5H_{11}OCH_2CH_2OCH_2CH_2O$)-8′-I-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**60**)[75]. The reaction of **54** with nitriles at 70–80 °C without solvent (acetonitrile) or in benzene (benzonitrile, acrylonitrile) followed by hydrolysis of the intermediate formed gives the corresponding amides [8-(RCONH)-8′-I-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (R = CH_3 (**61**), C_6H_5 (**62**), CH=CH_2 (**63**))[76]. Similar derivatives [8-Br-8′-L-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (L = SMe_2 (**64**), 1,4-dioxane (**65**)) were obtained by the reaction of **46** with $AlCl_3$ in benzene followed by treatment of the bromonium intermediate with the corresponding Lewis bases[74].

It should be noted that formation of the 8,8′-bridged derivatives, especially the charge-compensated ones, is one of characteristic features of the cobalt bis(1,2-dicarbollide) chemistry. The possible mechanism of these reactions was described as "electrophile-induced nucleophilic substitution" (EINS), which is characterized by the following processes: (i) the electrophilic particle removes the terminal hydrogen from the most electron-rich B–H vertex; (ii) the transient vacancy at this B-vertex is then filled by the most nucleophilic or most abundant particle present in the reaction medium[77].

Heating **1** with paraformaldehyde in acetic anhydride in the presence of sulfuric acid results in the formation of bridged oxonium derivative [8,8′-μ-(CH_3O)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**66**). Another oxonium derivative [8,8′-μ-(C_2H_5O)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**67**) was prepared by heating **1** in acetic anhydride in the presence of sulfuric acid. The isolated yields of the oxonium derivatives were small (20 and 5% for the methyl and ethyl derivatives, respectively)[78]. The methyloxonium derivative can be easily demethylated by Lewis acids. The structure of [8,8′-μ-(CH_3O)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] was confirmed by the X-ray structure analysis. The C_2B_9 pentagonal planes bound to the cobalt atom are non-parallel due to the short oxygen bridge (B–O = 1.50 Å, B(8)–O–B(8′) = 92°). The dihedral angle defined by these planes was found[79] to be 28°. In the structure of (Et_3MeN)[8,8′-μ-O-3,3′-Co(1,2-$C_2B_9H_{10})_2$], the monoatomic oxygen bridge causes the inclination of the C_2B_9 pentagonal planes by an angle of 28.3° (B–O = 1.461 Å)[80].

Compound [8,8′-μ-(CH_3CO_2)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**68**) was prepared by heating **1** in a 4 : 1 acetic acid–acetic anhydride mixture with $HClO_4$ as a catalyst. Hydrolysis of **68** in refluxing aqueous ethanol gives the diol

[8,8′-μ-$(HO)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**69**)[81]. The reaction of **1** with dimethyl sulfate at 80 °C in the presence of $AlCl_3$ results in the formation of [8,8′-μ-OSO_2O-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**70**). The structure of (Me_4N)-[8,8′-μ-OSO_2O-3,3′-Co(1,2-$C_2B_9H_{10})_2$] has been established by the X-ray diffraction. Both the dicarbollide ligands are 8,8′-bridged by sulfate ion (the distances B–O = 1.45 Å, O–S = 1.53 Å, S=O = 1.42 Å; the angels B–O–S = 127.6°, O–SO_2–O = 105.8°, and O=S=O = 116.5°). The dihedral angle between the C_2B_9 ligand planes equals[82] 3.9°. The oxonium derivative [8-{$O(CH_2CH_2)_2O$}-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**71**) was prepared by heating **1** in 1,4-dioxane at 80 °C in the presence of dimethyl sulfate and sulfuric acid. According to the data of X-ray structure analysis, the dicarbollide ligands in **71** have *cisoid* conformation[82]. γ-Irradiation of **1** in methanol produces asymmetrically bridged [8,8′-μ-(CH_2O)-3,3′-Co-(1,2-$C_2B_9H_{10})_2]^-$ (**72**)[83].

The reaction of the dimethylsulfoxonium salt [$(Me_2SO)_2H$][3,3′-Co-(1,2-$C_2B_9H_{11})_2$] with S_2Cl_2 in refluxing dichloromethane followed by alkaline methanolysis results in formation of the 8,8′-bridged sulfide derivative [8,8′-μ-S-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**73**)[84,85]. The same product was prepared by refluxing **1** with elemental sulfur and $AlCl_3$ in benzene[86]. Treatment of **73** with dimethyl sulfate in acetone gives the uncharged sulfonium derivative [8,8′-μ-(CH_3S)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**74**)[84,85]. This was also prepared by refluxing [8-(Me_2S)-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] with $AlCl_3$ in benzene ([8-Me_2S-8′-Cl-3,3′-Co(1,2-$C_2B_9H_{10})_2$] is a by-product)[85]. The alkylation of **73** with various alkyl halogenides in acetone affords high yields of the corresponding alkylsulfonium derivatives [8,8′-μ-(RS)-3,3′-Co-(1,2-$C_2B_9H_{10})_2$] (R = C_2H_5 (**75**), C_4H_9 (**76**), $CH_2C_6H_5$ (**77**), $CH_2CH{=}CH_2$ (**78**), $CH_2C{\equiv}CH$ (**79**))[85,87]. The [8,8′-μ-($HOOCCH_2S$)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] acid was prepared by the reaction of the sulfide derivative with sodium chloroacetate in alkaline methanol. Esterification of the acid with methanol in the presence of sulfuric acid gives [8,8′-μ-(CH_3OOCCH_2S)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**80**)[85]. Protonation of **73** with sulfuric acid in benzene or aqueous methanol generates a zwitterionic conjugated acid with a three-coordinated S-atom [8,8′-μ-(HS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**81**) (pK_a 3.18, 50% ethanol)[85,86]. The conjugated acid is very reactive. Its reaction with acrylonitrile in benzene reminds of the Michael addition giving [8,8′-μ-($NCCH_2CH_2S$)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**82**). The reaction of with paraformaldehyde in methanol produces [8,8′-μ-(CH_3OCH_2S)-3,3′-Co-(1,2-$C_2B_9H_{10})_2$] (**83**). In both cases, the reactions have a reversible character. In an alkaline medium the products decompose back to the parent compound **73**. On the other hand, **83** is converted during prolonged standing in methanol to the *S*-methyl derivative **74** (ref.[85]). The reaction of **73** with bromine in acetic acid yields an unstable [8,8′-μ-(BrS)-3,3′-Co-(1,2-$C_2B_9H_{10})_2$] derivative which is immediately converted with benzene in the presence of $AlCl_3$ into [8,8′-μ-(PhS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**84**)[85]. The structures of the alkylsulfonium derivatives [8,8′-μ-(CH_3OOCCH_2S)-3,3′-Co-(1,2-$C_2B_9H_{10})_2$] (ref.[88]) and [8,8′-μ-(HC≡CCH_2S)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (ref.[87]) were determined by X-ray diffraction analysis. The angles between the C_2B_9 planes of the ligands equal 16.6 and 16.5° for **83** and **79**, respectively (B–S = 1.925 and 1.918 Å for **83** and **79**, respectively).

The reaction of **1** with carbon disulfide in the presence of $AlCl_3$ and hydrogen chloride produces [8,8′-μ-(HCS_2)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**85**)[89,90]. The molecular structure of [8,8′-μ-(HCS_2)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] has been determined by single-crystal X-ray diffraction[89,91]. The two dicarbollide ligands are 8,8′-S-CH-S-bridged (the B–S bonds are 1.85 and 1.90 Å, the S–C bonds are 1.71 and 1.62 Å). The carborane ligands are essentially parallel, the dihedral angle defined by the C_2B_9 planes being only 2.3°. The reaction of **85** with sodium borohydride in ethanol gives [8,8′-μ-(H_2CS_2)-3,3′-Co-(1,2-$C_2B_9H_{10})_2]^-$ (**86**)[90]. Hydrolysis of **85** with 1 equivalent of alkali results in asymmetric breakage of the bridge giving [8-(HS)-8′-{H(O)CS-*S*}-3,3′-Co-(1,2-$C_2B_9H_{10})_2]^-$ (**87**)[90]. Acid and alkaline hydrolysis of **85** in refluxing aqueous ethanol gives the bis(sulfanyl) derivative [8,8′-$(HS)_2$-3,3′-Co-(1,2-$C_2B_9H_{10})_2]^-$ (**88**)[89,90]. The oxidation of the bis(sulfanyl) derivative **88** with hydrogen peroxide in alkaline medium results in formation of the disulfide [8,8′-μ-S_2-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**89**)[90]. The disulfide **89** was also prepared by heating Cs[3,3′-Co(1,2-$C_2B_9H_{11})_2$] with S_2Cl_2 in dichloromethane[85]. Methylation of the disulfide **89** with dimethyl sulfate in acetone gives [8,8′-μ-{S(Me)S}-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**90**) with the methyl group located on one of the sulfur atoms in the bridge. The treatment of **89** with bromine in acetic acid followed by reaction with $AlCl_3$ in benzene produces [8,8′-μ-{S(Ph)S}-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**91**)[85]. Refluxing the dimethylsulfoxonium salt [$(Me_2SO)_2H$][3,3′-Co(1,2-$C_2B_9H_{11})_2$] with acetic anhydride in benzene produces [8-(Me_2S)-3,3′-Co(1,2-$CoC_2B_9H_{10}$)(3′,1′,2′-$C_2B_9H_{11}$)] (**92**)[85]. The reaction of **1** with arenesulfenyl chlorides RSCl (R = C_6H_5, 2-$NO_2C_6H_4$) in acetonitrile gives [8-(RS)-3,3′-Co(1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11})]^-$ (R = C_6H_5 (**93**), 2-$NO_2C_6H_4$ (**94**)). The disubstituted derivative [8,8′-(4-$NO_2C_6H_4S)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**95**) is formed with 4-$NO_2C_6H_4SCl$ (ref.[92]).

The reaction of **1** with H_2SeO_3 in a benzene–acetic anhydride–sulfuric acid mixture followed by treatment with dimethyl sulfate produces

[8,8′-μ-(CH_3Se)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**96**). Similar reaction with elemental tellurium gives [8,8′-μ-(CH_3Te)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**97**). The isolated yields of the selenium- and tellurium-bridged cobalt bis(1,2-dicarbollides) were 8 and 3%, respectively[78].

The reaction of **1** with $NaNO_2$ in a benzene–sulfuric acid mixture produces mixture of [8,8′-μ-(NH_2)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**98**) (47%), [4,8′-μ-(NH_2)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**99**) (6%), and [8,8′-μ-{H_2NO-*N,O*}-3,3′-Co-(1,2-$C_2B_9H_{10}$)$_2$] (**100**) (21%)[78,93,94]. Methylation of **98** with dimethyl sulfate in a benzene–water mixture in the presence of potassium hydroxide gives [8,8′-μ-(MeNH)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**101**), whereas the reaction in aqueous solution produces [8,8′-μ-(Me_2N)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**102**)[78]. Treatment of **99** with dimethyl sulfate in alkaline ethanol produces [4,8′-μ-(Me_2N)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**103**)[93]. The enantiomers of **99** and **103** were separated by means HPLC on γ-cyclodextrin[93]. Alkylation of **98** with chloroacetic acid in methanolic potassium hydroxide solution followed by esterification of the acid formed with methanol and sulfuric acid results in [8,8′-μ-(CH_3OOCCH_2NH)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**104**). The structure of the compound was determined by single-crystal X-ray diffraction. The dicarbollide ligands are linked by a monoatomic nitrogen bridge to which a (methoxycarbonyl)methyl group is bound (B–N bond lengths are 1.577 and 1.563 Å). The angle between the open pentagonal faces of the dicarbollide ligands is 26.0° (ref.[95]).

Methylation of the oxime-bridged derivative **100** with methyl iodide in tetrahydrofuran in the presence of sodium hydride gives [8,8′-μ-(Me_2NO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**105**). The reaction of **100** with benzaldehyde and acetone in the presence of triethylamine produces the corresponding Schiff bases [8,8′-μ-(PhCH=NO-*N,O*)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**106**) and [8,8′-μ-(Me_2C=NO-*N,O*)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**107**). The treatment of **107** with 10% potassium hydroxide in ethanol gives the parent oxime **100**. Reduction of **100** with zinc dust and acetic acid in benzene results in the bridge cleavage giving [8-(H_3N)-8′-(HO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**108**). Methylation of this compound with dimethyl sulfate in ethanol in the presence of potassium hydroxide proceeds slowly giving mixture of [8-($MeNH_2$)-8′-(HO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**109**) (10%), [8-(Me_2NH)-8′-(HO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**110**) (17%), and [8-($MeNH_2$)-8′-(MeO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**111**) (57%). Compound **109** was also prepared by treatment of **100** with 10% potassium hydroxide in ethanol at 80 °C. The thermal disproportionation of **100** gives **110** (30%) and [8,8′-μ-(MeN=CH–O-*N,O*)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**112**) (40%)[94].

The reaction of **1** with white phosphorus in benzene at 80 °C in the presence of $AlCl_3$ followed by NaOH–dimethyl sulfate produces $[8,8'\text{-}\mu\text{-}(Me_2P)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (**113**) and $[8\text{-}(Me_3P)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**114**) isolated in 8 and 6% yields, respectively. The structure of the bridged derivative **113** has been established using X-ray diffraction analysis[96]. The inclination angle between both C_2B_9 ligand planes was found to be 11.6°.

The reaction of $K[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ with benzenediazonium tetrafluoroborate in refluxing benzene[4] or the decomposition of unstable benzenediazonium salt $(PhN_2)[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ in benzene[97] results in the 1,2-phenylene-bridged derivative $[8,8'\text{-}\mu\text{-}(1,2\text{-}C_6H_4)\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{10})_2]^-$ (**115**). This compound was also prepared by refluxing $Cs[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ with $AlCl_3$ in benzene[86]. The other product of this reaction is the cobaltacarborane sandwich complex with two 1,2-phenylene bridges between the dicarbollide ligands $[4,8'\text{:}8,4'\text{-di-}\text{-}\mu\text{-}(1,2\text{-}C_6H_4)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]^-$ (**116**)[98]. These compounds were erroneously identified as $[8,8'\text{-}\mu\text{-}(1,4\text{-}C_6H_4)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ and $[8,8'\text{-}Ph_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (ref.[99]). The structures of $K[8,8'\text{-}\mu\text{-}(1,2\text{-}C_6H_4)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[97]) and $Cs[4,8'\text{:}8,4'\text{-di-}\mu\text{-}(1,2\text{-}C_6H_4)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]$ (ref.[98]) were determined by single-crystal X-ray diffraction. The phenylene ring planes in **116** are mutually inclined by 72°. The Cs^+ cation is "sandwiched" between both phenylene rings.

The reaction of **1** with naphthalene at 80 °C in the presence of $AlCl_3$ produces the derivative with 1-methyleneinden-2-yl bridge $[8,8'\text{-}\mu\text{-}(CH_2\text{-}C_9H_6)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**117**). The structure of this derivative was unequivocally established by the X-ray diffraction study of $(Me_4N)\text{-}[8,8'\text{-}\mu\text{-}(CH_2\text{-}C_9H_6)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (ref.[100]).

Synthesis of derivatives with the toluene and 1,4-xylene bridges[4,99], as well as the reaction of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ with polystyrene[101] were described. Mesitylene, durene, as well as diphenyl oxide, triphenylbenzene, and biphenyl do not react[99] with $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$. The phenyl derivative $[8\text{-}Ph\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (**118**) was prepared by the reaction of **1** with dimethyl sulfate in benzene at 80 °C in the presence of concentrated sulfuric acid. The other product of this reaction is **70**. The structure of $(Me_4N)[8\text{-}Ph\text{-}3,3'\text{-}Co(1,2\text{-}CoC_2B_9H_{10})(1',2'\text{-}CoC_2B_9H_{11})]$ has been established by the X-ray diffraction. The dicarbollide ligands in the structure have *transoid* conformation[82]. The diphenyl derivative $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (**119**) was prepared by the reaction of $Na_2[3\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$ with $CoCl_2$ in tetrahydrofuran[102]. The hexamethyl derivative $[8,8',9,9',12,12'\text{-}Me_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$ (**120**) was prepared by the reaction of the hexaiodo derivative **53** with methylmagnesium bromide in refluxing tetrahydrofuran in the presence of $[Pd(Ph_3P)_2Cl_2]$ and CuI. According to the X-ray diffraction data, the dicarbollide ligands in the structure of $[8,8',9,9',12,12'\text{-}Me_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$ have *transoid* configuration[67]. The reaction of **1** with nitrobenzene at 80 °C in the presence of $AlCl_3$ produces $[8\text{-}(PhNO_2\text{-}O)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**121**) isolated in 9% yield[54].

The reaction of $Hg[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]_2$ with mercuric acetate in refluxing acetic acid gives[103] $Hg[9,9'\text{-}(CH_3OOCHg)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$. The reaction of **1** with mercuric acetate, trifluoroacetate, or tetrafluoroborate in water gives $[8\text{-}Hg\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**122**). Treatment of **122** with potassium chloride in aqueous acetonitrile results in $K[8\text{-}(ClHg)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**123**). The same product was isolated from the mercuration of **1** in acetonitrile or acetic acid followed by treatment with potassium chloride. The disubstituted derivative $K[8,9'(12')\text{-}(ClHg)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (**124**) was prepared under the same conditions using the excess of the mercurating agent. Treatment of **124** with silver nitrate gives $[8,9'(12')\text{-}Hg_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2](NO_3)$ (**125**)[104].

It should be noted that the pictured above prismatic *cisoid* and antiprismatic *transoid* conformations are the limiting positions for possible free rotation of the dicarbollide ligands[85]. The prefered conformation of the dicarbollide ligands in non-bridged cobalt bis(1,2-dicarbollide) derivatives depends mainly on the electron interaction of substituents on the dicarbollide ligands and the dicarbollide carbon atoms. For instance, in structure of **118**, attraction between the slightly positive C–H vertices of the unsubstituted dicarbollide ligand and the slightly negative phenyl ring (attached to the most negative B(8) vertex) results in *transoid* conformation. On the other hand, in the structure of **71**, the repulsion between the analogous C–H vertices and the positively charged oxonium group in the dioxane substituent give rise to *cisoid* configuration. In some cases, the dicarbollide ligand conformation can be determined by steric interaction of substituents in the dicarbollide ligands.

All investigated single-atom bridged species (**66**, **79**, **83**, **104**, **113**) have prismatic *cisoid* conformation caused by geometric restrictions. The inclination angle decreases in the series of bridges OR > NR_2 > SR > PR_2. The same conformation was found for the diatomically bridged compound **115**. The compounds with triatomic bridges (**70**, **85**, **117**) have staggered (*cis* antiprismatic) conformation.

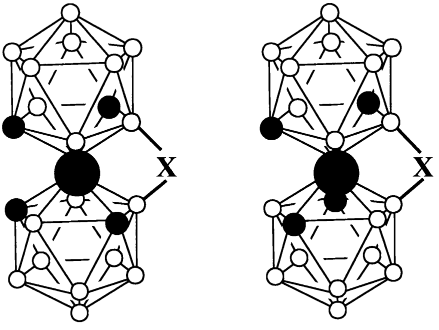
3. DERIVATIVES OF $[2,2'\text{-Co}(1,7\text{-}C_2B_9H_{11})_2]^-$

Compound $[1,1',7,7'\text{-Ph}_4\text{-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_9)_2]^-$ (**126**) was prepared in 50% yield in the reaction of $[7,9\text{-Ph}_2\text{-}7,9\text{-}C_2B_9H_9]^{2-}$ with $CoCl_2$ in refluxing 1,2-dimethoxyethane–diglyme mixture[54].

The reaction of **2** with formaldehyde in a mixture of concentrated hydrochloric acid and chloroform at 60 °C gives in high yield $[6,6'\text{-}\mu\text{-(MeO)-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]$ (**127**) (Fig. 4). The oxonium derivative can be easily demethylated by Lewis bases, *e.g.* by methanol[105].

The reaction of **2** with elemental sulfur in benzene at 60 °C in the presence of $AlCl_3$ gives the sulfide derivative $[6,6'\text{-}\mu\text{-S-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]^-$ (**128**). The structure of $(Ph_4P)[6,6'\text{-}\mu\text{-S-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]$ has been established by single-crystal X-ray diffraction. The dihedral angle between both C_2B_9 pentagonal ligand planes was found[106] to be 12.2°. Methylation of the sulfide with dimethyl sulfate in aqueous solution produces $[6,6'\text{-}\mu\text{-(MeS)-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]$ (**129**)[107]. The alkylsulfonium derivatives $[6,6'\text{-}\mu\text{-(RS)-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]$ (R = C_2H_5 (**130**), C_3H_7 (**131**), i-C_3H_7 (**132**), n-C_4H_9 (**133**), n-C_6H_{13} (**134**), $CH_2CH{=}CH_2$ (**135**)) were prepared by alkylation of the sulfide **128** with the corresponding alkyl halogenides in propan-2-ol. The reaction of **128** with chloroacetic acid in an aqueous sodium carbonate solution followed by esterification of the resulting acid with methanol and $SOCl_2$ produces derivative $[6,6'\text{-}\mu\text{-}(CH_3OOCCH_2S)\text{-}2,2'\text{-Co-}(1,7\text{-}C_2B_9H_{10})_2]$ (**136**)[105].

The reaction of **2** with $NaNO_2$ in a mixture of benzene and sulfuric acid results in $[6,6'\text{-}\mu\text{-}(H_2N)\text{-}2,2'\text{-Co}(1,7\text{-}C_2B_9H_{10})_2]$ (**137**) (pK_a 10.1, 50% aqueous ethanol). The treatment of the amine **137** with dimethyl sulfate in 10% so-



racemic meso

X =		
	OMe	**127**
	SMe	**129**
	SEt	**130**
	SPr	**131**
	SPr-i	**132**
	SBu	**133**
	SC_6H_{13}	**134**
	$SCH_2CH{=}CH_2$	**135**
	SCH_2COOCH_3	**136**
	NH_2	**137**
	NMe_2	**138**
	NHMe	**139**
	PMe_2	**140**

FIG. 4
6,6′-Single-atom-bridged cobalt bis(1,7-dicarbollide) derivatives

dium hydroxide gives [6,6′-μ-(Me_2N)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (**138**). The monomethylamino derivative [6,6′-μ-(MeNH)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (**139**) was prepared by the treatment of a benzene suspension of (Me_4N)[6,6′-μ-(HN)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] precipitated from 10% aqueous hydroxide with methyl iodide[105].

All prepared oxo-, thia-, and aza-bridged derivatives are enantiomeric mixtures: 6,11′-μ-*meso* isomers are completely missing in the reaction products. The resolution of the enantiomers of all bridged cobalt bis(1,7-dicarbollides) was performed by HPLC on β-cyclodextrin[108].

The reaction of **2** with white phosphorus in benzene at 80 °C in the presence of $AlCl_3$ followed by treatment with dimethyl sulfate in the presence of sodium hydroxide produces [6,6′-μ-(Me_2P)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (**140**) and [6-(Me_3P)-2,2′-Co(1,7-$C_2B_9H_{10}$)(1′,7′-$C_2B_9H_{11}$)] (**141**) isolated in 8 and 6% yields, respectively. The structures of both compounds were determined by single-crystal X-ray diffraction[96]. The dihedral angle between the C_2B_9 pentagonal ligand planes is 6.6°. The reaction of **2** with carbon disulfide in the presence of $AlCl_3$ and hydrogen chloride produces [μ-(HCS_2)-2,2′-Co-(1,7-$C_2B_9H_{10}$)$_2$] (**142**)[90].

An original approach to the synthesis of bridged derivatives of cobalt bis(1,7-dicarbollide) was proposed by Hawthorne *et al.* The reaction of 2 equivalents of *closo*-1,8-$C_2B_9H_{11}$ with sodium salt of pyrazole in benzene gives a mixture of [10,10′-μ-(pyrazol-1-yl-2-yliumyl)-(*nido*-7,9-$C_2B_9H_{10}$)$_2$]$^-$ and [10,11′-μ-(pyrazol-1-yl-2-yliumyl)-(*nido*-7,9-$C_2B_9H_{10}$)$_2$]$^-$ (*meso* and racemic forms, respectively). The reaction of this mixture with $CoCl_2$ in alkaline aqueous solution produces the corresponding mixture of [6,6′-μ-(pyrazol-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (racemic form) (**143**) and [6,11′-μ-(pyrazol-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (*meso* form) (**144**) which can be separated by preparative TLC techniques or by column chromatography[109]. Compounds [6,6′-μ-(pyrazol-4-carboxylic acid-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (**145**) and [6,11′-μ-(pyrazol-4-carboxylic acid-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] (**146**) were prepared in a similar way starting from methyl pyrazole-4-carboxylate[109,110]. The molecular structures of [6,6′-μ-(pyrazol-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] and of [6,11′-μ-(pyrazol-1-yl-2-yliumyl)-2,2′-Co(1,7-$C_2B_9H_{10}$)$_2$] were determined from the single-crystal X-ray diffraction experiments[109,110]. Due to the tight bridging of the planar pyrazole moiety, the bonding faces of the dicarbollide ligands are eclipsed. The angles between normals to the two bonding planes are 6.6 and 6.2° for **143** and **146**, respectively. The approach developed was used for the synthesis of the ^{57}Co radionuclide-containing cobaltacarborane [μ-(pyrazol-4-carboxylic acid-1-yl-2-yliumyl)-

2,2′-Co(1,7-$C_2B_9H_{10})_2$] for radioimmunodiagnostics. The cobaltacarborane prepared was conjugated to anti-carcinoembryonic antigen monoclonal antibody T84.66 with full retention of immunological activity. Biodistribution studies in nude mice bearing carcinoembryonic antigen-producing tumors showed excellent localization of the conjugate in tumors[109–112].

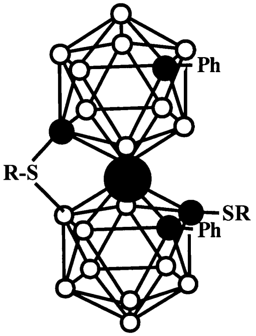
4. OTHER COBALT BIS(DICARBOLLIDES)

The unusual B,C′-bridged mixed-ligand cobalt bis(dicarbollides) [1,8′-μ-(RS)-2-(RS)-1,9′-Ph_2-3,3′-Co(1,2-$C_2B_9H_8$)(1′,9′-$C_2B_9H_9$)] (R = Me (**147**), Et (**148**), and Bu (**149**)) were isolated as by-products (yields 10, 10, and 11%, respectively) from the synthesis of the corresponding cobalt bis(1,2-dicarbollides) [1,1′-$(RS)_2$-2,2′-Ph_2-3,3′-Co(1,2-$C_2B_9H_9)_2]^-$ (reaction of [7-Ph-8-(RS)-7,8-$C_2B_9H_{10}]^{2-}$ with $CoCl_2$ in refluxing 1,2-dimethoxyethane). The structure of [1,8′-μ-(EtS)-2-(EtS)-1,9′-Ph_2-3,3′-Co(1,2-$C_2B_9H_8$)(1′,9′-$C_2B_9H_9$)] was established by single-crystal X-ray diffraction[53].

5. POTENTIAL APPLICATIONS OF COBALT BIS(DICARBOLLIDES)

Detailed analysis of possible applications of cobalt bis(dicarbollides) is beyond the scope of this review and will be mentioned only briefly. A more detailed recent review on this subject was given in ref.[113].

The use of cobalt bis(1,2-dicarbollide) for solvent extraction of radionuclides is the most studied. This compound as well as its halogeno derivatives were found to be extremly robust, withstanding strong acids,



R = Me **147**
Et **148**
Bu **149**

FIG. 5
Structure of [1,8′-μ-(RS)-2-(RS)-1,9′-Ph_2-3,3′-Co(1,2-$C_2B_9H_8$)(1′,2′-$C_2B_9H_9$)]

moderate bases, high temperatures, and intense radiation[114,115]. The first application of the cobalt bis(1,2-dicarbollide) to solvent extraction of radionuclides was reported more than 20 years ago[116]. The principally new extraction reagent has been investigated in solvent extraction and so far, more than 100 papers and patents have been published on the subject. A variety of nuclides, both radioactive and stable (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+; Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}, Pd^{2+}, Pb^{2+}; lanthanides, *etc.*) can be successfully separated and isolated using cobalt bis(dicarbollide) and its derivatives. The most recent references on this subject are[51,52,54,117–123]. Another direction in the cobalt bis(dicarbollide) application is its use in electrochemistry for transfer of cations from water to organic solvents and across lipid membranes, and as components of ion-selective electrodes[124–130]. Lithium cobalt bis(1,2-dicarbollide) was found to be an effective catalyst for the conjugate addition of silyl ketene acetals to hindered α,β-unsaturated carbonyl compounds and for the substitution of allylic acetates with various nucleophiles[131–132].

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