

THE STRUCTURE OF $[6,6'-\mu\text{-S}(1,7\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]\text{[PPh}_4\text{]}^+$ Jaromir PLESEK^{al}, Andreas FRANKEN^{al} and Roland FROHLICH^b^a *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic; e-mail: ^lvlckova@iic.cas.cz*^b *Organisch-Chemisches Institut der Universitat, 48149 Munster, Germany*

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Single crystal X-ray structure of monoatomically bridged $[6,6'-\mu\text{-S}(1,7\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]\text{[PPh}_4\text{]}^+$ is reported and selected bond lengths and angles are tabulated. A distinctly smaller dihedral angle (12.2°) between both pentagonal ligand planes than found earlier in the formally related symmetric analogue $8,8'-\mu\text{-MeOCOCH}_2\text{S}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-3-Co}$ (16.5°) is discussed. This is the first reported X-ray structure of a monoatomically bridged cobaltacarborane with nonadjacent carbon atoms in deltahedral ligands.

Key words: S-Bridged cobaltacarborane with nonadjacent C-atoms, structure; Inclination of ligand planes.

A series of prochiral monoatomically bridged cobaltacarborane derivatives of the $[2\text{-Co-(1,7-C}_2\text{B}_9\text{H}_{11})_2]^-$ ion with the bridging moiety spanning the B6 and B6' positions has been synthesized and resolved into enantiomers¹⁻³.

So far, these compounds have been characterized only by mass spectroscopy and multinuclear NMR spectroscopy. Although their constitution has been established beyond any doubt, the question of mutual inclination of both pentagonal ligand planes of both deltahedral ligands still remained.

Recently we succeeded in growing some good crystals of the salt $[6,6'-\mu\text{-S}(1,7\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]\text{[PPh}_4\text{]}^+$ and subjected it to crystallographic investigation. The found X-ray structure is presented in Fig. 1, selected bond lengths and angles including the dihedral interligand angle, relevant to the discussion, are listed in Tables I and II.

RESULTS AND DISCUSSION

A distinct mutual inclination of both pentagonal ligand planes in all monoatomically bridged metallacarboranes of the $8,8'-\mu\text{-R-E}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-3-M}$ type has been reported (Table III) but so far there was no information on whether a nonadjacent position of carbon atoms in monoatomically bridged cobaltacarboranes might change this picture.

The dihedral angle between both pentagonal ligand planes found now in the title species (12.2°) is appreciably smaller than that found earlier⁶ in a related symmetric

analogue with adjacent carbon atoms in deltahedral ligands (16.5° , *cf.* Table III), although the general geometry of the parent ions $[2\text{-Co-(1,7-C}_2\text{B}_9\text{H}_{11})_2]^-$ and $[3\text{-Co-(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$ is essentially the same.

TABLE I
Selected bond lengths (in Å) in the anion $[6,6'\text{-}\mu\text{-S-(1,7-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]^-$

Bonds	Lengths	Bonds	Lengths
C1–B6	1.722(7)	B6'–S	1.875(6)
C1–B3	1.685(7)	B6–Co	2.032(5)
C7–B3	1.670(7)	B11–Co	2.074(5)
C7–B11	1.673(7)	C7–Co	2.098(5)
B6–B11	1.811(7)	B3–Co	2.071(6)
C1'–B6'	1.712(8)	C1–Co	2.071(5)
C1'–B3'	1.693(9)	B6'–Co	2.024(6)
C7'–B3'	1.647(9)	B11'–Co	2.076(5)
C7'–B11'	1.666(8)	C7'–Co	2.089(5)
B6'–B11'	1.800(9)	B3'–Co	2.054(7)
B6–S	1.870(5)	C1'–Co	2.049(7)

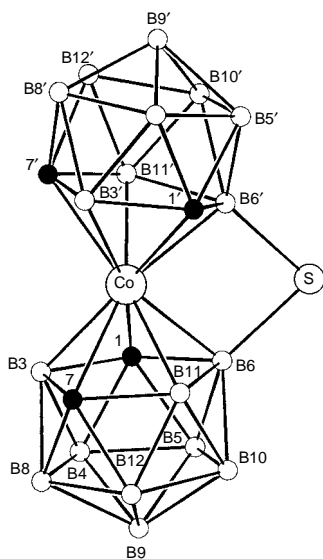


FIG. 1
Structure of $[6,6'\text{-}\mu\text{-S-(1,7-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]^- [\text{PPh}_4]^+$

The geometric parameters related to the Co and S-bridge in both compounds are compared in Fig. 2 and Table IV.

It seems that the $(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2^-$ ligands accommodate to the "natural" lengths and internal angle of the sulfur bridge more easily than their $(1,7\text{-C}_2\text{B}_9\text{H}_{11})_2^{2-}$ counterpart. The smaller dihedral angle found in the title ion is compensated by a slight distortion of the B6–Co–B6', Co–B6–S and B6–S–B6' angles along with distinct shortening (2.5%) of the B6–S bond*.

TABLE II
Selected angles (in °) in the anion $[6,6'\text{-}\mu\text{-S-(1,7-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]^-$

Atoms	Angles	Atoms	Angles
C1–B6–B11	103.4(3)	B11–Co–C1'	89.4(2)
B6–B11–C7	107.0(4)	C7–Co–B3'	100.3(2)
B11–C7–B3	110.9(4)	B3–Co–C7'	99.8(2)
C7–B3–C1	107.3(4)	C1–Co–B11'	88.3(2)
B3–C1–B6	110.9(4)	B6–Co–B6'	75.7(2)
C1'–B6'–B11'	103.2(4)	Co–B6–S	100.5(3)
B6'–B11'–C7'	107.0(4)	B6–S–B6'	83.3(3)
B11'–C7'–B3'	111.6(4)	S–B6'Co	100.6(3)
C7'–B3'–C1'	106.8(4)	Dihedral angle	12.2
B3'–C1'–B6'	110.9(4)	between ligand planes	

TABLE III
Dihedral angles in $8,8'\text{-}\mu\text{-R-E(1,2-C}_2\text{B}_9\text{H}_{10})_2\text{-3-M}$ metallocarboranes

R–E<M	Me–O<CO	Me–O<Fe	CH ₃ OCOCH ₂ S<Co	CH ₃ OCH ₂ NH<Co	Me ₂ P<Co
Dihedral angle, °	28.3	31.2	16.5	28	11.6
Reference	4	5	6	7	8

* A complete set of structural parameters has been sent to the Fachinformationszentrum Karlsruhe, 76344 Eggenstein, Leopoldshafen Data Base; e-mail: crysdata@fiz-karlsruhe.de.

The structure of the title compound confirms the constitution inferred previously only from multinuclear NMR data supported by chiral resolution¹. As in all monoatomically bridged cobaltacarboranes investigated so far, the deltahedral ligand plane pentagons are eclipsed. Of course, the carbon atoms are not eclipsed, as shown by successful resolutions into enantiomers¹ (Fig. 1).

Our study represents the first X-ray structure of a monoatomically bridged metallacarborane with nonadjacent carbon atoms within the deltahedral ligands.

EXPERIMENTAL

Preparation of Monocrystals of $[6,6'\text{-}\mu\text{-S}(1,7\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]^-\text{[PPh}_4\text{]}^+$

The bridged anion was prepared as described by us previously¹. Its PPh_4^+ salt was precipitated with PPh_4Cl from aqueous solution of the corresponding sodium salt, the precipitate was collected, dried on air overnight, dissolved in dichloromethane, filtered and layered with three volumes of hexane in an NMR tube. The deep-brown crystals were collected after 10 days, washed with diethyl ether and dried *in vacuo* (135 Pa, 20 °C, 4 h).

TABLE IV

Important distances and angles in formally related monoatomically bridged cobaltacarboranes

Compound	Angles, °				Distances, pm	
	α	β	γ	δ	<i>a</i>	<i>b</i>
$[6,6'\text{-}\mu\text{-S}(1,7\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-2-Co}]^-$	12.2	83.3	100.5	75.7	203.2	187
$8,8'\text{-}\mu\text{-RS}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-3-Co]$	16.5	82.8	100.3	76.6	204.1	192.5

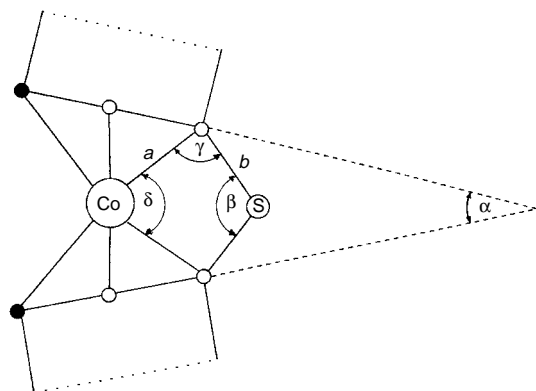


FIG. 2
Bond lengths and angles in the bridge area in monoatomically bridged cobaltacarboranes

Single Crystal X-Ray Diffraction Analysis

The crystallographic measurement was made on an Enraf–Nonius Mach3 diffractometer operating in the $\omega/2\theta$ mode using graphite-monochromated MoK α -radiation. The structure was determined using standard heavy atom methods and refined by full-matrix least squares⁹. All non-hydrogen atoms were refined with anisotropic thermal parameters, the cluster hydrogen atoms were located by Fourier difference synthesis and refined riding with coupled isotropic thermal parameters¹⁰.

Crystal data for [6,6'- μ -S(1,7-C₂B₉H₁₀)₂-2-Co][PPh₄]⁺, $M = 693.14$, monoclinic, space group $P2_1/n$, $a = 11.092(1)$, $b = 11.526(1)$, $c = 28.654(4)$ Å, $\beta = 100.64(1)^\circ$, $V = 3\,599.2(7)$ Å³, $Z = 4$, $D_c = 1.279$ Mg/m³, $\mu = 6.0$ cm⁻¹, $F(000) = 1\,424$, $R = 0.0635$, $wR^2 = 0.1819$ for refinement of 7 286 unique absorption-corrected (via Ψ scan data) reflections with $I > 2\sigma(I)$.

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