

**A [8,8'-μ-I-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] METALLACARBORANE COMPLEX  
WITH A IODONIUM BRIDGE. EVIDENCE  
FOR A BROMONIUM ANALOGUE**

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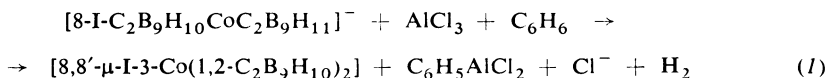
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The [8,8'-μ-I-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] complex with a iodonium bridge between both dicarbollide ligands was prepared and its constitution was established by NMR methods. It behaves as a Lewis acid opening its bridge by the action of Lewis bases to form [8-I-8'-L-3-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] species. The less stable bromonium analogue was not isolated but its existence was confirmed by the reaction with Lewis bases affording the [8-Br-8'-L-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] derivatives.

A family of bridged [8,8'-μ-X-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] complexes with X = O, S, Se, Te and N as bridging atoms has been discovered and its chemistry developed in our laboratory during the last decade<sup>1-6</sup>. Constitution of the corresponding compounds was established beyond any doubt by spectral methods. Fine structural details were revealed by X-ray diffraction studies<sup>7,8</sup> on two of the very numerous representatives of this series. We wish to report herein the synthesis of a unique member of this family with a monoatomic iodonium bridge between both dicarbollide ligands.

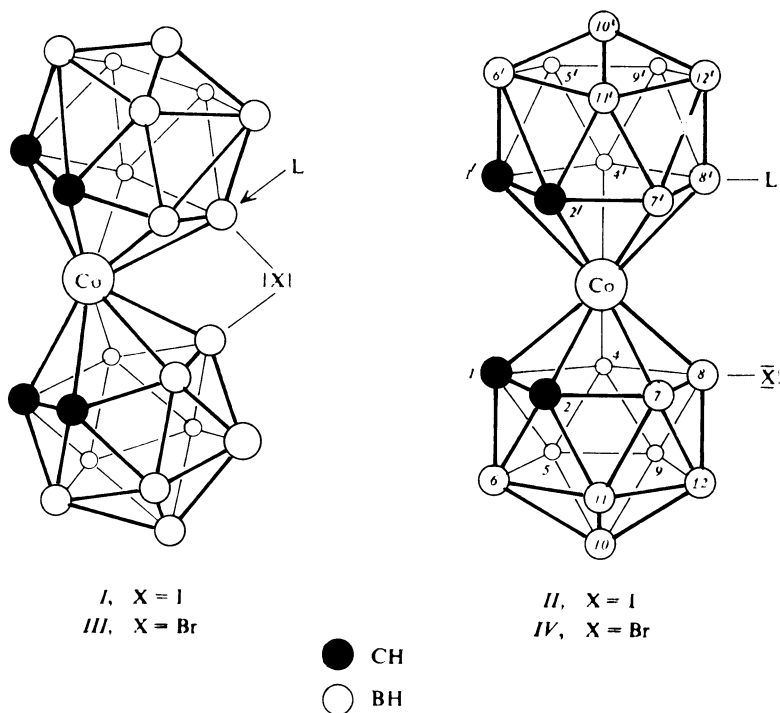
An interligand bridge[8,8'-μ-iodonium-3-commo-3-cobalta-bis-(1,2-dicarbocloso-dodecaborane)](22) complex, [8,8'-μ-I-3-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (*I*) (see Scheme) can be obtained in good yield according to the scheme:



A possible reaction mechanism consists in an abstraction of the hydride ion from the B<sub>(8')</sub> vertex by the C<sub>6</sub>H<sub>6</sub>.AlCl<sub>3</sub> complex to form compound *I* after occupying the vacant B<sub>(8')</sub> orbital with one of the nonbonding electron pairs of the terminal 8-iodine atom.

The structure of the complex *I*, shown in Scheme, is consistent with its mass (*m/z* 452) and <sup>1</sup>H NMR data indicating the expected molecular cut-off and the presence of four equivalent CH groups. Consistent with the proposed C<sub>2v</sub> symmetry is also

the <sup>11</sup>B NMR spectrum exhibiting the 1 : 2 : 2 : 2 : 1 patterns of doublets along with one singlet of intensity 1 associated with the iodonium bridge substituted B<sub>(8,8')</sub> atoms. The <sup>11</sup>B NMR spectrum is almost identical with that of the previously reported<sup>2</sup> 8,8'-μ-CH<sub>3</sub>Te analogue. The iodonium bridge, although never observed in metallocene or metallaborane chemistry, has its long known counterpart in the well developed chemistry of diaryliodonium salts even though their synthesis under the conditions of electrophilic substitution is unknown. Grushin and co-workers<sup>9,10</sup> have recently reported the preparation of arylcarboranyl and bis-carboranyl iodonium and bromonium salts.



Complex *I* behaves as a Lewis acid to form with Lewis bases a family of uncharged [8-I-8'-L-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (*II*) compounds [L = (CH<sub>3</sub>)<sub>2</sub>S, *IIa*; C<sub>5</sub>H<sub>5</sub>N, *IIb*; (CH<sub>3</sub>)<sub>3</sub>N, *IIc* and NH<sub>3</sub>, *IId*] the properties of which are given in Table I. Nucleophilic attack of the base at the B<sub>(8')</sub> site results in opening the iodonium bridge whereby the iodine atom remains as the B<sub>(8)</sub> terminal group. The reaction is probably sterically controlled as demonstrated by reaction times increasing in the series (CH<sub>3</sub>)<sub>2</sub>S < C<sub>5</sub>H<sub>5</sub>N, NH<sub>3</sub> < (CH<sub>3</sub>)<sub>3</sub>N at room temperature. No other species with a monoatomic interligand bridge could so far be opened by Lewis bases.

A strong indication points even to the existence of a species with a bivalent bromo-

mium bridge —  $[8,8'\text{-}\mu\text{-Br-3-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (*III*) even though we were unable to isolate it in pure state. Complex *III* is detectable by TLC as a red spot, drifting with a 86% travel velocity of its iodinium congener *I*, and gradually disappearing due to an easy hydrolysis of *III* by the residual humidity of the silica gel. Isolation of compound *III* was unsuccessful since the benzene solution obtained in the reaction contained a salt like species with the  $\text{Al}^{3+}$  cation which could not be separated without destructing the desired compound *III*.

Nevertheless, on adding bases to the freshly prepared benzene solution of complex *III* the colour turns orange and the complexes  $[8\text{-Br-8'-L-3-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (*IV*) [ $\text{L} = (\text{CH}_3)_3\text{S}$ , *IVa* and  $\text{C}_4\text{H}_8\text{O}_2$ , *IVb*] can be isolated as individual uncharged compounds (for properties see Table I) structurally analogous to complexes *II*.

### EXPERIMENTAL

$^{11}\text{B}$  NMR spectra were recorded at 64.18 MHz with a Varian XL-200 spectrometer and were externally referenced to  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  (positive  $\delta$  values downfield).  $^1\text{H}$  NMR spectra were obtained at 60 MHz on a Tesla BS-467 spectrometer and were internally referenced to tetramethylsilane. Low resolution mass spectral data were collected using a GC/MS HP 5985 instrument at 70 eV. Melting points were determined in sealed capillaries and are uncorrected. TLC was performed on Silufol silica gel sheets (producer Kavalier Votice, Czechoslovakia). All reactions were performed under dry nitrogen unless otherwise stated. The starting  $[8\text{-X-1,2-C}_2\text{B}_9\text{H}_{10}\text{-3-Co-1',2'-C}_2\text{B}_9\text{H}_{11}]^- \text{Cs}^+$  complexes ( $\text{X} = \text{Br}, \text{I}$ ) were prepared according to the previously described procedure<sup>11</sup>. Benzene and dioxane were distilled from  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ , pyridine and dimethylsulphide from solid potassium hydroxide prior to use. All other commercially available reagents were used as purchased.

TABLE I  
Properties of the  $[8\text{-X-8'-L-3-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  complexes

Compound	X	L	$m/z$	m.p. ( $0^\circ\text{C}$ )	$R_F^a$	$^1\text{H NMR}^b$		$^{11}\text{B NMR}^{b,c}$		
						$\text{CH}_{\text{skel.}}$	$\text{CH}_{\text{lig.}}$	$\text{B}_{(8)}$	$\text{B}_{(8')}$	
<i>IIa</i>	I	$(\text{CH}_3)_2\text{S}$	515	247–255	0.52	4.61	4.93	2.72	–1.85	7.07
<i>IIb</i>	I	$\text{C}_5\text{H}_5\text{N}$	531	335–337	0.36	4.57	4.76	10.00	–2.18	14.90
<i>IIc</i>	I	$(\text{CH}_3)_3\text{N}$	511	286–288	0.30	4.86	5.11	3.25	–2.50	17.98
<i>IId</i>	I	$\text{H}_3\text{N}$	469	308–309	0.10	4.47	4.63	—	–3.20	10.96
<i>IVa</i>	Br	$(\text{CH}_3)_2\text{S}$	468	266	0.45	4.56	4.78	2.71	12.85	7.37
<i>IVb</i>	Br	$\text{C}_4\text{H}_8\text{O}_2$	494	260 <sup>d</sup>	0.29	4.45	4.81	4.13	12.30	23.40
								4.81		

<sup>a</sup> In benzene; <sup>b</sup> in hexadeuterioacetone; <sup>c</sup> singlets of the substituted B atoms, the rest of the spectrum consists of 16 overlapped doublets; <sup>d</sup> decomposition in solid state.

Preparation of [8,8'- $\mu$ -I-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (*I*)

Finely powdered [8-I-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-3-Co-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> Cs<sup>+</sup> (11.6 g; 0.02 mol) and AlCl<sub>3</sub> (6.6 g; 0.05 mol) in benzene (60 ml) were heated at 80°C for 40 min. Hydrogen with some HCl evolved during the procedure and the solution turned dark red. The mixture was allowed to cool to room temperature for 1 h, cyclohexane (60 ml) was added and, after 5 min stirring, the solid was filtered and washed with two 10 ml portions of benzene-cyclohexane (1 : 1). To the red filtrate silica gel (5 g) was added to absorb the Al salts and, after 5 min stirring, the dark silica gel was sucked off. The organic solvents were stripped off from the filtrate *in vacuo* leaving a solid residue which was treated with three 10 ml portions of chloroform and the chloroform extract was sucked off after a short contact with the solid. The insoluble red powder was dried at 50°C/1.3 Pa to yield 5.0 g (55%) of TLC pure compound *I*, not melting up to 350°C but decomposing above 250°C; *m/z* 452 (corresponding to <sup>12</sup>C<sub>4</sub><sup>11</sup>B<sub>8</sub><sup>1</sup>H<sub>20</sub><sup>59</sup>Cl<sup>127</sup>I<sup>+</sup>); *R<sub>F</sub>* (benzene-hexane 1 : 2) 0.33; <sup>1</sup>H NMR spectrum (hexadeuteriobenzene):  $\delta$  2.32 (s, CH skel.); <sup>11</sup>B NMR spectrum (hexadeuteriobenzene)  $\delta_B$  2.35(1B, d, B<sub>(10)</sub>), -6.35(2B, d, B<sub>(4,7)</sub>), -7.23(2B, d, B<sub>(9,12)</sub>), -15.0(2B, d, B<sub>(5,11)</sub>), -16.3(1B, s, B<sub>(8)</sub>), -23.0(1B, d, B<sub>(6)</sub>).

Preparation of [8-I-8'-L-3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (*II*) Compounds

[L = (CH<sub>3</sub>)<sub>2</sub>S, *Iia*; C<sub>5</sub>H<sub>5</sub>N, *Iib*; (CH<sub>3</sub>)<sub>3</sub>N, *Iic* and NH<sub>3</sub>, *Iid*] In a typical experiment, to a solution of the iodonium complex *I* (0.45 g; 10<sup>-3</sup> mol) in benzene (20 ml), 0.005 mol of the relevant Lewis base in benzene (10 ml) were added. In the case of ammonia, the benzene solution of *I* was stirred under this gaseous base. The progress of all reactions was monitored by TLC and the reactions were continued until the red spot of the starting compound disappeared. All volatiles were then evaporated *in vacuo* at ambient temperature, the residue was dissolved in benzene (c. 30 ml) and chromatographed on a silica gel column (30 × 2.5 cm) in benzene to develop orange bands of the products. The individual compounds were isolated on evaporating the benzene from pure fractions, washing the residue with two 5 ml portions of cyclohexane and drying it at 25°C/1.3 Pa. The following yields of compounds *II* (for properties see Table I) were obtained: *Iia*, 0.42 g (81.7%) with dimethyl sulphide; *Iib*, 0.37 g (69.6%) with pyridine; *Iic*, 0.35 g (68.3%) with trimethylamine; *Iid*, 0.36 g (76.9%) with ammonia. To complete the reactions, 0.5, 4, 24 and 4 h were required, respectively.

*In situ* Preparation of [8,8'- $\mu$ -Br-3-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] and its Reactions with Lewis Bases

Finely powdered [8-Br-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>-3-Co-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> Cs<sup>+</sup> (5.4 g; 0.01 mol) and anhydrous AlCl<sub>3</sub> (3.9 g; 0.03 mol) in benzene (30 ml) were stirred at room temperature for 3 h. Some gas evolved and the solution turned brick red to develop a bright red spot on TLC (benzene-hexane 1 : 2, *R<sub>F</sub>* 0.29). The spot gradually faded during the TLC experiment and after 5 min it completely disappeared leaving a yellow trail behind. The filtrate was divided into two parts after sucking off the solid. The first portion was treated with dimethyl sulphide (3 ml) and the second one with dioxane (5 ml). In both cases the solution turned orange to separate some voluminous material. After standing for 30 min at ambient temperature, the mixtures were worked up in the following manner: The solutions were decanted, all solvents were evaporated *in vacuo*, the residues were dissolved in benzene (c. 30 ml) and purified chromatographically as in the preceding experiment to give 0.65 g (27.9%) and 0.5 g (20.4%) of the *IVa* and *IVb* complexes with dimethyl sulphide and dioxane, respectively. Further characteristics of the products are summarized in Table I.

The <sup>1</sup>H and mass spectra were recorded by Dr F. Mareš and Dr Z. Weidenhoffer, both of the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague. We would like to thank these colleagues for their kind assistance.

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