UNUSUAL REARRANGEMENT OF NAPHTHALENE IN THE SYNTHESIS OF A NOVEL B8-B8-BRIDGED DERIVATIVE IN THE $[(1,2\text{-}C_2B_9H_{11})_2\text{-}3\text{-}Co]^-$ SERIES. X-RAY STRUCTURE AND ^{11}B NMR SPECTRA of $[8,8'\text{-}\mu\text{-}(CH_2\text{–}C_9H_6)\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^-$ $(CH_3)_4N^+$

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On treatment of the $[(1,2\text{-}C_2B_9H_{11})_2Co]^-$ ion with naphthalene in presence of $AlCl_3$ a remarkably bridged $[8,8'\text{-}\mu\text{-}(CH_2\text{–}C_9H_6)\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^-$ ion is obtained as a single isolated compound. The triatomic $\text{–}CH_2\text{–}C_9H_6\text{–}$ bridge is derived from the rearranged naphthalene nucleus. The mechanism of this reaction is obscure but it does resemble the "Electrophile-Induced Nucleophilic Substitution" reported earlier. The structure of the compound was established by multinuclear NMR spectroscopy and by single crystal X-ray diffraction.

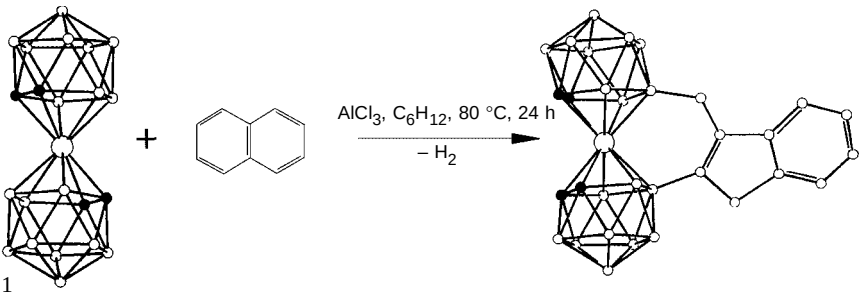
Key words: Rearrangement of naphthalene; Cobaltacarborane with triatomic bridge; X-Ray diffraction; Multinuclear NMR spectroscopy.

Some time ago we have reported on a quite curious bridging of the $[3\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ ion **1** with the *o*-phenylene group on reaction of the cesium salt of **1** with benzene and aluminium chloride[1]. Recently a still more surprising twofold arylene bridges have been constructed under slightly more forcing conditions[2]. On the other hand, replacing aluminium chloride with a more complex and milder catalytic system (dimethyl sulfate–H_2SO_4) we were able to introduce a single phenyl group to the 8-position of **1** without any bridge formation[3]. The possible mechanisms of these "Electrophile-Induced Nucleophilic Substitutions" (EINS, ref.[4]) has been discussed in the respective papers.

RESULTS AND DISCUSSION

Here we report on a very surprising outcome of an attempt to repeat the same reactions with naphthalene and aluminium chloride carried out in cyclohexane as a solvent (Scheme 1). Although this reaction might be of the same general EINS type as were those described earlier, we do not understand completely the real sequence of events. It is apparent that the rearrangement of naphthalene is rather indirect, possibly occurring

within the transient $C_{10}H_9^-$ ion (formed *e.g.* by a hydride ion transfer from the most negative B(8)-H vertex *via* $[HAlCl_3]^-$ ion). We have no direct experimental evidence for this or another reaction course. However, the curious complex **2** with a triatomic bridge is the single isolated product of this reaction, and hydrogen evolution was observed. We are not aware of any other reported case of such "Naphthalene Ring Contraction".



SCHEME 1

The ^1H and ^{11}B evidence clearly revealed the unusual constitution of the new bridged species: Two C-H carborane signals of equal intensity 2 were compatible with two nonequivalent 8-X-1,2-$C_2B_9H_{10}$ and 8′-Y-1′,2′-$C_2B_9H_{10}$ ligands sandwiching the Co(III) ion. The same was evident from the ^{11}B NMR spectrum, consisting of two patterns $1^s : 1 : 2 : 2 : 2 : 1$ typical of B(8,8′) substituted 1,2(1′,2′)-$C_2B_9H_{10}$ ligands. Signals of all eighteen boron vertices along with the relevant terminal hydrogen signals were resolved (with only one overlap in the highest field signal) and unequivocally assigned. The nature of the bridging group could be inferred from the ^1H NMR spectrum using the signal of the Me_4N^+ ion at 3.45 ppm (12) as internal standard. The complex pattern at the lowest field apparently belongs to the four nearly equivalent C–H vertices of the phenylene ring whereas the sharp singlets of intensity 2 at 2.16 ppm and 2.067 ppm, respectively, indicate the presence of two CH_2 groups.

Only the species in Fig. 1 can show such NMR spectral features. Any signals of crystallization solvent were absent. Because there was a direct evidence for all 40 hydrogens (and indirect for all 18 C-atoms) and for all 18 B-atoms, we considered an elemental analysis unnecessary, moreover the structure could be directly established by X-ray diffraction.

The X-ray diffraction confirmed this unexpected result (Fig. 1) and afforded some additional features. Here we present only crystallographic parameters of the measured crystals (Experimental), atomic coordinates and selected bond lengths and angles* (Tables I and II).

* The complete set of X-ray data has been sent to the Fachinformationszentrum Karlsruhe, 76344 Eggemstein, Leopoldshafen Data Base; e-mail: crysdata@fiz-karlsruhe.de.

Characteristic features of the new structure are: (i) antiprismatic conformation of both pentagonal ligand planes; (ii) their negligible mutual inclination; (iii) the shortest distances within the pentagonal ligand planes unequivocally reveal the location of both intraligand carbon pairs; (iv) the shortest distance within the tricarbon bridge (C4–C12) reflects the presence of a localized double bond in the bidentate indenemethylene moiety.

In all so far investigated single-atom bridged species (O, refs[6–8]; N, refs[6,9]; S, refs[5,6,10]) and diatomically bridged compouds (arylene[1,2]; S–S, ref.[5]) an eclipsed (prismatic) conformation has been found, whereas a staggered (antiprismatic) conformation is typical of compounds with triatomic bridges (SCHS, refs[11,12]; OSO_2O, ref.[3]). The same staggered conformation has been found now also in compound **2** (Fig. 1).

The new compound is not only the first cobaltacarborane with a three-membered carbon bridge between B8 and B8′ as bridgeheads, but it also documents an unprecedented " reductive ring contraction" affecting one ring of naphthalene.

EXPERIMENTAL

Apparatus

^{1}H (500 MHz) and ^{11}B (160.4 MHz) NMR spectra were recorded in hexadeuterioacetone on a Varian XL-500 spectrometer, chemical shifts are given in δ (ppm referenced to tetramethylsilane and $BF_3O(C_2H_5)_2$, positive spectra downfield). X-Ray diffraction was carried out on CAD4, Enraf–Nonius device.

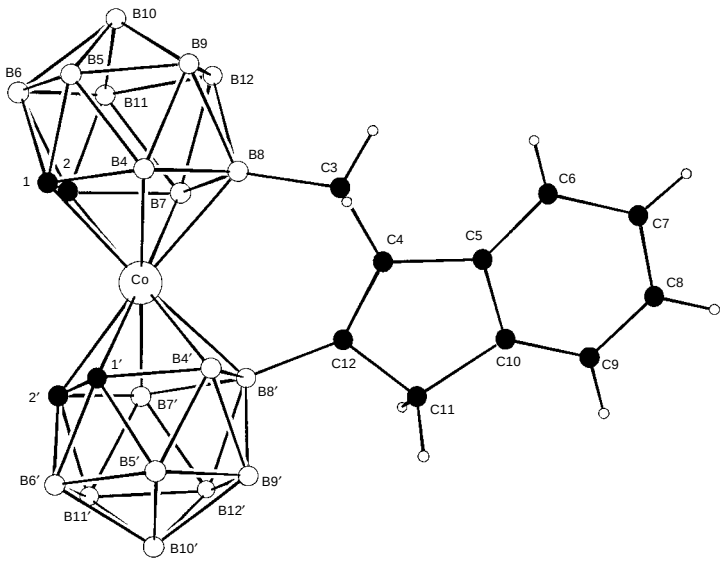


FIG. 1
X-Ray crystal structure of cobaltacarborane **1**

Preparation of $[8,8'\text{-}\mu\text{-}(CH_2\text{–}C_9H_6)\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^-\ NMe_4^+$

A mixture of $Cs[1,2\text{-}(C_2B_9H_{11})_2\text{-}3\text{-}Co]$ (2.3 g, 5 mmol), naphthalene (20 g, 150 mmol) and $AlCl_3$ (1.4 g, 10 mmol) in cyclohexane (80 ml) was stirred at 80 °C for 24 h. The mixture turned red during the reaction; after cooling, the solid was separated and washed with cyclohexane (3 × 20 ml). The residue contained a mixture of unreacted starting material (TLC) and some $CsAlCl_4/AlCl_3$. The combined cyclohexane phases were poured on a column of silica gel (200 g) and washed with hexane (200 ml). After drying *in vacuo*, the colored band of the column is eluted with acetone, the acetone evaporated *in vacuo* and the residue was dissolved in acetonitrile–chloroform 1 : 3. For the final separation, the solution was transferred to a column containing 300 g silica gel and eluted with the same solvent mixture. The first fraction consists of undefined zwitterions. The second main orange band was mechanically separated and extracted with acetone. Acetone was removed *in vacuo* and the residue was dissolved in aqueous ethanol (50 ml). The tetramethylammonium salt was precipitated from this solution by 0.1 M $(CH_3)_4NCl$ (10 ml) and the precipitate was recrystallized from hot 70% ethanol to give 0.53 g (20%) of the title salt. ^{11}B NMR: 22.136 s, 1 B (B8); 14.200 s, 1 B (B8′); –0.074 d, 1 B, J = 2.919 (B10′); –2.319 d, 1 B, J = 2.802 (B10); –4.432 d, 2 B, J = 2.013 (B4,B7); –5.288 d, 2 B, J = 2.129 (B4′,B7′); –5.288 d, 2 B, J = 2.745 (B9′,B12′); –7.153 d, 2 B, J = 2.773 (B9,B12); –17.811 d, 2 B, J = 1.650 (B5,B11); –18.515 d, 2 B, J = 1.520 (B5,B11); –25.404 d, 2 B (B6,B6′).

TABLE I
Selected bond lengths (in Å) in the $[8,8'\text{-}\mu\text{-}(CH_2\text{–}C_9H_6)\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-}Co]^-$ anion

Atoms	Bond lengths	Atoms	Bond lengths
C1–C2	1.60(2)	B7′–Co	2.086(15)
C1–B4	1.68(2)	B8′–Co	2.097(13)
B4–B8	1.83(2)	B4′–Co	2.092(14)
B8–B7	1.85(2)	B8–C3	1.58(2)
B7–C2	1.66(2)	C3–C4	1.46(2)
C1′–C2′	1.61(2)	C4–C5	1.52(2)
C1′–B4′	1.67(2)	C4=C12	1.33(2)
B4′–B8′	1.83(2)	C5–C6	1.40(2)
B8′–B7′	1.81(2)	C5–C10	1.37(2)
B7′–C2′	1.68(2)	C6–C7	1.41(2)
C1–Co	2.028(12)	C7–C8	1.36(2)
C2–Co	2.037(12)	C8–C9	1.32(2)
B7–Co	2.07(2)	C9–C10	1.33(2)
B8–Co	2.126(4)	C10–C11	1.55(2)
B4–Co	2.10(2)	C11–C12	1.53(2)
C1′–Co	2.018(13)	C12–B8′	1.58(2)
C2′–Co	2.038(12)		

^{1}H NMR: 3.865 s and 3.832 s, 2 H (H-carb.); 7.303, 7.206, 7.157 and 6.958 m, 1 H (H-arom.); 2.161 s and 2.067 s, 2 H (CH_2); 3.450 s, 12 H ($4 \times CH_3$).

Preparation of the Monocrystals

The $N(Me)_4$ salt was dissolved in hot aqueous ethanol and after 24 h the deep orange-red crystals were collected and dried *in vacuo* (135 Pa, 20 °C, 4 h).

Single-Crystal X-Ray Diffraction Analysis

Crystallographic data were obtained on an Enraf–Nonius X-CAD4 Turbo diffractometer operating in the $\omega/2\theta$ mode using graphite-monochromated MoKα-radiation. The structure was determined by standard heavy-atom methods and refined by full-matrix least squares[13]. All non-hydrogen atoms were refined with anisotropic thermal parameters, the cluster hydrogen atoms were located on a Fourier difference synthesis and refined with individual isotropic thermal parameters.

Crystal data $B_{18}C_{18}H_{40}NCo$: M_r = 524, orthorhombic, space group *Pbca* (No. 61), a = 12.8950 (15), b = 15.013 (4), c = 29.873 (4) Å, (based on the least squares refinement of 25 precisely centered

TABLE II
Selected bond angles (in °) in the [8,8′-μ-(CH_2–C_9H_6)-(1,2-$C_2B_9H_{10}$)$_2$-3-Co]$^-$ anion

Atoms	Angles	Atoms	Angles
C1–C2–B7	113.2(10)	C3–C4–C5	120.3(14)
C2–B7–B8	105.1(11)	C4–C5–C10	108.1(15)
B7–B8–B4	103.9(10)	C5–C10–C11	106.9(15)
B8–B4–C1	105.2(12)	C10–C11–C12	105.9(13)
B4–C1–C2	112.5(11)	C11–C12–C4	106.2(14)
C1′–C2′–B7′	112.7(10)	C12–C4–C5	112.8(14)
C2′–B7′–B8′	105.1(12)	C4–C5–C6	130.3(16)
B7′–B8′–B4′	104.7(10)	C5–C6–C7	115.5(12)
B8′–B4′–C1′	105.2(10)	C6–C7–C8	119.3(14)
B4′–C1′–C2′	112.3(10)	C8–C9–C10	119.3(15)
B4–Co–B4′	92.2(7)	C9–C10–C11	132.3(16)
C1–Co–C1′	97.0(5)	C9–C10–C5	120.7(13)
C2–Co–C2′	98.5(5)	C10–C11–C12	105.9(13)
B7–Co–B7′	91.7(7)	C11–C12–C4	106.2(14)
B8–Co–B8′	91.3(6)	C4–C12–B8′	128.4(13)
Co–B8–C3	122.6(10)	C11–C12–B8′	124.4(14)
Co–B8′–C12	118.4(9)	Dihedral angle	2.02
C3–C4–C12	126.6(13)	between ligand planes	

reflections within the 2.09–20.01θ range), V = 5 783.2 (17) Å^3, Z = 8, D_c = 1.123 g cm^{-3}, μ = 0.603 mm^{-1}, $F(000)$ = 1 896.

Measurement: A crystal 0.3 × 0.35 × 0.2 mm in size was measured on a CAD4 diffractometer (MoKα radiation, λ = 0.71069 Å). Of a total of 5 252 reflections up to 2θ = 40° within the *h*, *k*, *l* range of –12,12; –4,14; –2,28, respectively, 2 701 were regarded as "observed" according to the $I > 2\sigma(I)$ criterion. Three standard reflections, which were monitored every 90 min showed no significant fluctuations (<2.6%).

Structure solution and refinement: direct methods[13] (SHELXS86), full-matrix least squares refinement[14] (SHELXL93), anisotropic refinement of all non-hydrogen atoms, hydrogen atoms fixed in calculated positions. Function minimized: $w(F_o^2 - F_c^2)^2$ with, $w = 4F^2/[(F_o^2)]^2$ final R = 0.0639, R_{int} = 0.1085, S = 0.884, $|(\Delta/\sigma)_{max}|$ = 0.074. The final difference electron density map was featureless, with extremal values of 0.557; –0.215 e Å^3 near the Co atom. Program ORTEP (ref.[15]) was used to draw the molecules.

NMR spectra were measured by Dr J. Fusek of the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Prague.

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