SYNTHESIS AND PROPERTIES OF COBALTACARBORANES WITH SUBSTITUTED MONOATOMIC BRIDGES BETWEEN LIGANDS OF THE 6,6′-μ-$R_nE(1,7\text{-}C_2B_9H_{10})_2$-2-Co TYPE

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Syntheses, properties and constitutions of eleven asymmetric cobaltacarboranes with various substituents on monoatomic bridges between both ligands of the type 6,6′-μ-$R_nE(1,7\text{-}C_2B_9H_{10})_2$-2-Co (E = O, R = methyl; E = S, R = ethyl, propyl, isopropyl, allyl, butyl, hexyl and CH_3OCOCH_2; E = N, R = H (H), methyl, (H), and dimethyl) are described. Constitution assignation of all compounds are based on ^{1}H and ^{11}B NMR spectroscopy experiments complemented by ^{11}B-^{11}B COSY NMR and mass spectrometry; UV-VIS, melting points and TLC parameters are also presented. Only the racemic forms were obtained, although in principle, the *meso*-forms might result as well.
Key words: Boranes, chiral; Cobaltadicarbollides, bridged; Metallaboranes.

The first metallacarborane complex with an intramolecular monoatomic bridge between ligands was synthesized in this Institute more than twenty years ago[1]. Subsequently, we have found out that it was only the first representative of an extensive family of compounds with the general formula 8,8′-μ-$R_nE(1,2\text{-}C_2B_9H_{10})_2$-3-Co (type **1**; E = bridging atom, *e.g.* O, S, Se, Te, N, and I, R = alkyl; for O, S, Se, Te, and I, n = 1, for N, n = 2 (for schematic structure see Fig. 1). About thirty species of type **1** have been prepared and characterized[2–5]. Structures of several representatives of **1** were determined by X-ray diffraction[6–9]. The most interesting features found in this study are an unprecendented prismatic eclipsed conformation of both pentagonal ligand planes and their appreciable inclination. However, all compounds of the type **1** possess at least one plane of symmetry.

Recently, we described the syntheses and constitution of the first representatives of another family of isomeric compounds with general formula 6,6′-μ-$R_nE(1,7\text{-}C_2B_9H_{10})_2$-2-Co (type **2**, E = bridging atom, R = alkyl) (Fig. 2). Compounds **2a** and **2b** contained a monosulfur bridge, their constitution was proposed on the basis of NMR data, supplemented by mass spectrometry and confirmed by chiral resolution of their enentiomers by HPLC on β-cyclodextrin column[10]. Characteristic feature of the type **2** family is a rigid helical arrangement of the ligand planes (Fig. 2) and consequent protochirality.

Here we report on syntheses and properties of a series of compounds with these structures with various bridging atoms and various alkyl groups attached to them. These species were prepared as substrates for a study of chiral resolution by HPLC on β-cyclodextrin columns[11]. The ^{11}B and ^{1}H NMR, UV-VIS, mass spectrometry and other data are listed in Tables I–IV.

Compounds **2c–2i** were prepared by conventional alkylations of the cesium salt of the **2a** anion[10] by reactions with corresponding alkyl halogenides in refluxing isopropyl alcohol and were characterized by ^{11}B NMR (Table I), mass and UV-VIS spectroscopy, R_F values, melting points (Table II) and ^{1}H NMR shifts (Table III). Noteworthy is an appreciable decrease in reaction rate of these alkylations compared to those observed earlier within the isomeric family[4] of compounds **1**.

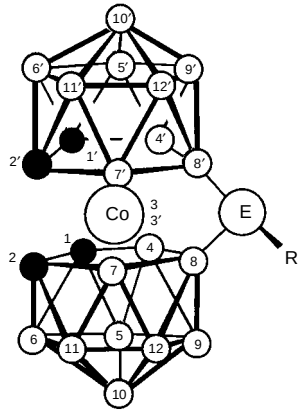


FIG. 1
Schematic representation of symmetric bridged metallaboranes [8,8′-μ-R_nE(1,2-$C_2B_9H_{10})_2$-3-Co] (R = alkyl, E = S, O, n = 1; E = N, n = 2). Terminal hydrogens are omitted for clarity

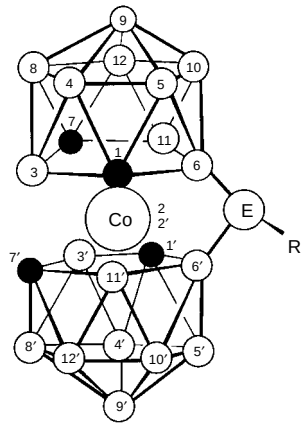
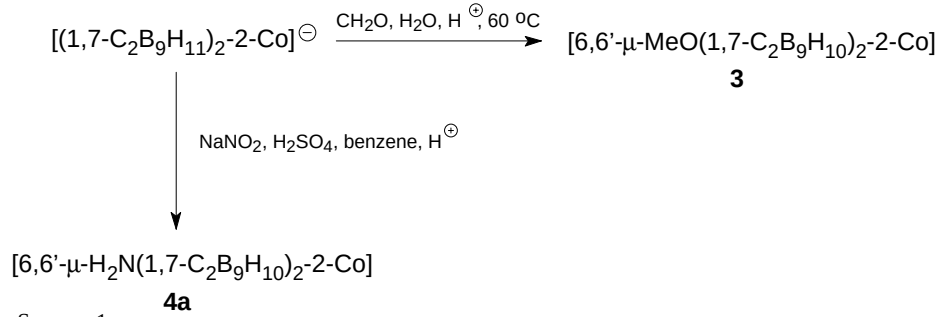


FIG. 2
Schematic representation of asymmetric bridged metallaboranes [6,6′-μ-R_nE(1,7-$C_2B_9H_{10})_2$-2-Co] (R = alkyl, E = S, O, n = 1; E = N, n = 2). Terminal hydrogens are omitted for clarity

Syntheses of species **3** and **4** with oxygen and nitrogen bridges were carried out as in the case of related compounds[2] by reaction of $[(1,7\text{-}C_2B_9H_{11})_2\text{-}2\text{-}Co]^{(-)}$ (ref.[12]) with sodium nitrite or formaldehyde in the presence of a strong acid, according to Scheme 1.



SCHEME 1

Both reactions apparently proceed *via* hydride abstraction from the most reactive boron atoms in 6,6′ positions of the $[(1,7\text{-}C_2B_9H_{11})_2\text{-}2\text{-}Co]^{(-)}$ skeleton by strong acid followed by attack by a nucleophile particle. Such specific reaction mechanism called "nucleophilic reaction under electrophilic conditions" (ref.[2]) is common for a broad range of *closo*-borate and *closo*-metallaborate anions.

In all cases, only the racemic forms of **3** and **4** were obtained; the respective *meso*-forms were completely missing, apparently for the same reason as discussed[10] earlier. Recent X-ray diffraction[14] confirmed its structure.

The compound **3** behaves as a true oxonium salt, *i.e.* it can be easily demethylated by almost any Lewis base, *e.g.* by methanol[11]. The same demethylation was already observed earlier[2] on the isomeric compound related to type **1**.

The hydrogens at the $H_2N<$ bridge in **4a** are relatively acidic (pK_{a1} 10.1, see Experimental) in constrast to the isomer of **1** series which was proved to be neutral[2].

Methylation of ion **4a** is much faster than that of **2a** ion and only the *N*,*N*-dimethyl derivative **4c** was formed under usual conditions. Therefore, a special procedure must be used for preparation of the monomethyl derivative **4b** (for details, see Experimental).

Structural Studies

The arrangement of ligands around the bridging atoms in the **2**,**3** and **4** type compounds is apparently tetrahedral, similarly to that in the closely related **1** series[9]. This fact brings about some difficulties in the NMR signals assignment. In the **2** series, only in the case of anion **2a** with naked bridge atom[10] or related compounds **4a** and **4c** with identical *exo*-skeletal ligands on the bridge, both deltahedral ligands are magnetically equivalent. In such case, two CH carborane signals should be observed in ^1H NMR spectrum and nine ^{11}B signals are expected in the ^{11}B NMR spectrum. However, in all

other species, *e.g.* **2b–2i**, **3** and **4b**, the substituents at the bridging atom induce a magnetic nonequivalence in both deltahedral ligands and, consequently, four CH carborane signals should appear in the ^{1}H NMR and 18 ^{11}B signals should be expected in the ^{11}B NMR spectrum. On the other hand, the presence of such large number of boron signals in a relatively narow spectral range often leads to one or several coincidence overlaps in the spectrum. The problem was discussed in detail in the previous paper[10]. Complex, NMR spectrum should constitute an evidence that only the racemic form is present but, on the other hand, it complicates the assignment of the respective signals to the relevant vertices. This is why the ^{11}B NMR chemical shifts of **2c–2i** and **3** are summarized in Table I with no assignment for particular boron atoms. However, a close relation of spectral

TABLE I
^{11}B NMR data[a] ((δ, ppm), intensity *i*, and *J*(B,H), Hz (in parentheses)) of sulfur and oxygen bridged species

Compound	Bridge	δ, *i* (*J*(B,H))
2c	EtS<	1.61, 2 B (150); –2.82, 2 B (156); –8.81, 2 B (173); –10.88, 3 B (156); –11.99 s, 1 B; –12.59 s, 1 B; –13.47, 2 B (150); –15.22, 3 B (156); –17.15, 1 B (162); –17.72, 1 B (162)
2d	PrS<	1.54, 2 B (150); –2.83, 2 B (156); –8.85, 2 B (164); –10.88 d, 3 B; –11.87 s, 1 B; –12.50 s, 1 B; –13.49, 2 B (147); –15.2, 3 B (162); –17.15, 1 B (162); –17.70, 1 B (164)
2e	iPrS<	1.77, 2 B (149); –2.36, 2 B (159); –8.28, 1 B (116); –8.98, 1 B (113); –10.49 d, 1 B; –10.88 d, 2 B; –12.26 s, 2 B; –13.15 d, 1 B; –13.61 d, 1 B; –15.17 d, 3 B; –16.99 d, 1 B; –17.94 d, 1 B
2f	AllylS<	1.60, 2 B (146); –2.83, 2 B (159); –8.79, 2 B (162); –10.88, 3 B (153); –10.88, 3B (153); –11.89 s, 1 B; –12.50 s, 1 B; –13.51, 2 B (146); –15.17, 3 B (156); –17.17, 1 B (162); –17.68, 1 B (165)
2g	BuS<	1.58, 2 B (147); –2.80, 2 B (156); –8.79 2 B (162); –10.85, 3 B (156); –11.84 s, 1 B; –12.46 s, 1 B; –13.47, 2 B (147); –15.19, 3 B (159); –17.13, 1 B (159); –17.68, 1 B (162)
2h	HexS<	1.58, 2 B (147); –2.81, 2 B (156); –8.80, 2 B (162); –10.84, 3 B (156); –11.85 s, 1 B; –12.50 s, 1 B; –13.47, 2 B (147); –15.19, 3 B (159); –17.17, 1 B (162); –17.68, 1 B (162)
2i	MeAcS<	1.66, 2 B (147); –3.01, 2 B (159); –8.81, 2 B (159); –10.83, 3 B (165); –11.97 s, 1 B; –12.60 s, 1 B; –13.42 d, 2 B; –15.17, 3 B (156); –17.13, 1 B (162); –17.62, 1 B (161)
3	MeO<	5.10 s, 2 B; 4.02 d, 1 B; –0.59 d, 1 B; –1.597, 2 B (143); –2.59 d, 1 B; –6.95, 1 B (165); –10.33 d, 1 B; –10.77 d, 1 B; –11.89, 1 B (171); –13.09, 1 B (142); –14.25, 1 B (156); –15.01, 1 B (143); –17.20, 1 B (146); –18.61, 1 B (150); –19.26 d, 1 B; –20.08, 1 B (143)

[a] s, singlet; d, doublet (in cases when *J*(B,H) could not be assigned due to overlaps).

patterns of **2c–2i** and **3** species to the already reported anion[10] [6,6′-μ-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co]$^{(-)}$ can be clearly seen from Table I and the ^{11}B NMR chemical shift intercorrelation diagram in Fig. 3.

The much simpler spectra of **4a** and **4c**, with both substituents on nitrogen bridge identical, are very similar exhibiting nine boron signals due to the above discussed magnetic equivalence of both ligands. The assignment of all boron signals could be made on the basis of ^{11}B-^{11}B COSY NMR data. Also, ^{11}B NMR signal assignment of ten peaks of **4b** with asymmetrically substituted nitrogen bridge has been possible, due

TABLE II
Some characteristic properties of bridged cobaltaboranes **2**, **3** and **4**

Compound	M.p., °C	R_F	MS, *m/z*	UV-VIS, λ (ε)			
2c	159	0.37[a]	386	208	225 sh	292	439
		0.16[b]		(37 500)	(21 600)	(51 600)	(800)
2d	124	0.43[a]	400	206	225 sh	295	439
		0.19[b]		(36 200)	(19 000)	(49 000)	(780)
2e	127	0.41[a]	400	206	225 sh	294	440
		0.18[b]		(37 100)	(22 100)	(48 800)	(680)
2f	158	0.39[a]	398	207	226 sh	294	439
		0.15[b]		(37 300)	(22 900)	(49 700)	(760)
2g	95	0.47[a]	414	207	226 sh	293	439
		0.22[b]		(37 500)	(22 400)	(49 000)	(790)
2h	–	0.53[a]	442	207	226 sh	293	439
		0.26[b]		(37 400)	(22 200)	(48 900)	(760)
2i	142	0.08[a]	430	207	235 sh	294	438
		0.01[b]		(27 200)	(23 000)	(48 500)	(780)
3	194	0.31[a]	356	207	240 sh	287	422
		0.11[b]		(36 000)	(16 400)	(38 300)	(2 500)
4a	>360	0.14[c]	341	206	–	280	432
				(35 000)		(31 500)	(2 100)
4b	180	0.04[a]	355	206	228 sh	281	432
		0.34[c]		(36 300)	(17 500)	(30 800)	(1 200)
4c	215	0.21[a]	369	205	–	281	432
		0.62[c]		(33 200)		(31 300)	(2 100)

[a] Benzene–hexane 1 : 2. [b] Hexane–dichloromethane (9 : 1). [c] Benzene.

to close similarity of the spectra of all three nitrogen bridged derivatives (see Table IV and Fig. 3).

The ^{1}H NMR data of all compounds under discussion are presented in Table III. As expected (see above), only two CH signals can be seen in ^{1}H spectra of compounds **4a** and **4c** with symmetrically substituted nitrogen bridge. All other bridged compounds

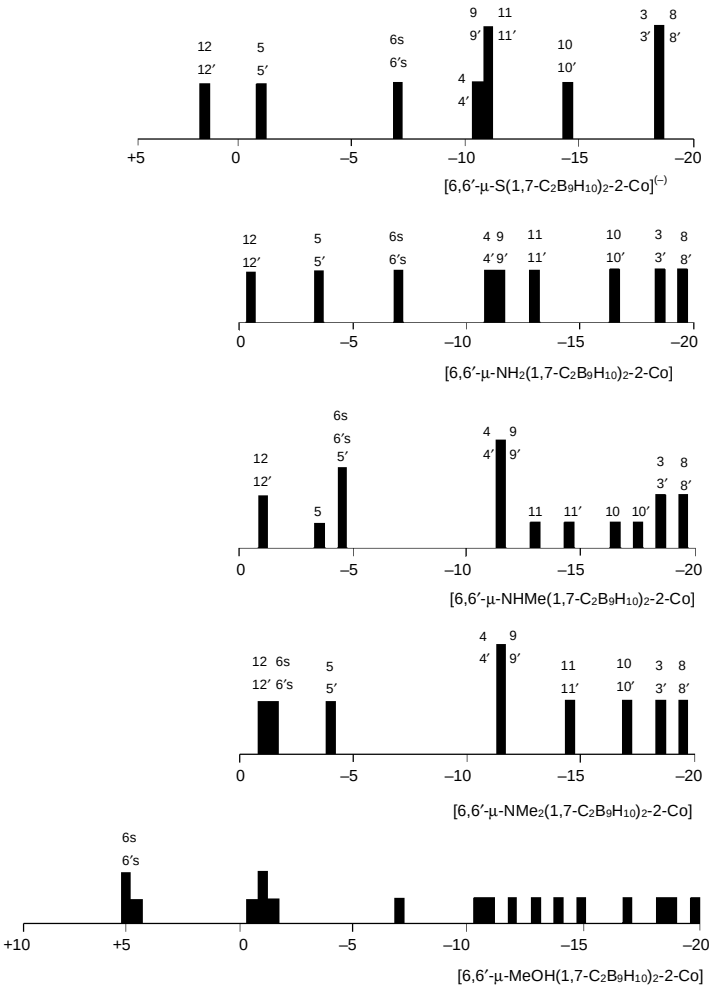


FIG. 3

Intercorrelation diagram of ^{11}B NMR chemical shifts of [6,6′-μ-S(1,7-$C_2B_9H_{10})_2$-2-Co]$^{(-)}$, 6,6′-μ-Me_2N(1,7-$C_2B_9H_{10})_2$-2-Co and 6,6′-μ-CH_3O(1,7-$C_2B_9H_{10})_2$-2-Co derivatives

exhibit expected four CH signals due to magnetic nonequivalence of ligands, with exception of **2e** and **4b** species with one coincidental overlap.

All the compounds, the synthesis of which was described in this paper, were successfully resolved into enantiomers by HPLC on β-cyclodextrin chiral stationary phases (CSPs). The study based on availability of a large variety of type **2**, **3** and **4** compounds have brought a substantial contribution to the current knowledge of stereochemical aspect influence on separation on these CSPs[10,11,13].

EXPERIMENTAL

TLC were performed on silica gel sheets (Silufol, Kavalier, Czech Republic). The chemicals used were of reagent grade (Lachema, Brno, Czech Republic), unless stated otherwise and were used as purchased.

The ^{1}H and ^{11}B NMR spectra (δ, ppm) were measured on a Varian XL-500 spectrometer at 500 MHz (^{1}H) and 160.4 MHz (^{11}B) in deuterioacetone. ^{1}H chemical shifts were measured relative to the residual protons from the lock solvent and referenced to tetramethylsilane (0.0 ppm). ^{11}B chemical

TABLE III
^{1}H NMR shifts of the 6,6′-μ-$R_nE(1,7\text{-}C_2B_9H_{10})_2$-2-Co (E = S, O, n = 1; E = N, n = 2) bridged species

Compound	δ, ppm	
	B–H	C–H
2c	3.10 1 H; 3.22 2 H; 4.04 1 H	1.55 t, 3 H (CH_3); 3.05 m, 2 H (CH_2S)
2d	3.22 1 H; 3.23 1 H; 4.06 1 H; 4.30 1 H	1.10 t, 3 H (CH_3); 1.90 m, 2 H (CH_2); 2.99 m, 2 H (CH_2S)
2e	3.18 2 H; 4.03 1 H; 4.31 1 H	1.57 t, 6 H (CH_3); 3.51 m, 1 H (CHS)
2f	3.12 1 H; 3.23 1 H; 4.05 1 H; 4.32 1 H	3.72 m, 2 H (CH_2S); 5.50 m, 2 H (CH_2=); 5.59 m, 1 H (=CH)
2g	3.12 1 H; 3.23 1 H; 4.05 1 H; 4.29 1 H	1.00 t, 3 H (CH_3); 1.49 m, 2 H (CH_2); 1.77 m, 2 H (CH_2CH_2S); 2.98 m, 2 H (CH_2S)
2h	3.12 1 H; 3.23 1 H; 4.05 1 H; 4.29 1 H	0.91 t, 3 H (CH_3); 1.32 m, 6 H (CH_2); 1.83 m, 2 H (CH_2CH_2S); 2.99 m, 2 H (CH_2S)
2i	3.15 1 H; 3.24 1 H; 4.09 1 H; 4.26 1 H	3.85 s, 3 H (CH_3O); 3.81 s, 2 H (O_2CCH_2S)
3	2.00 1 H; 2.82 1 H; 4.22 1 H; 4.53 1 H	4.11 s, 3 H (CH_3N)
4a	2.96 2 H; 4.23 2 H	4.49 brs, 2 H (H_2N)
4b	2.93 2 H; 4.09 1 H; 4.16 1 H	2.74 brs, 3 H (CH_3NH); 4.82 brs, 1 H (NH)
4c	2.95 2 H; 3.98 2 H	2.81 brs (CH_3N)

shifts were measured relative to $BF_3 . OEt_2$ with $B(OCH_3)_3$ as internal standard (in a capillary inserted into the sample tube, 18.1 ppm). UV-VIS spectra were measured on a PU 8720 spectrometer (Philips, Cambridge, U.K.) in methanolic solutions in quartz cells with optical length 1 cm. Melting points were measured in sealed capillaries on the Kofler stage. pK_a of **4a** derivative was obtained by acidimetric titration in 50% ethanol using an OP 506 pH meter (Radelkis, Budapest, Hungary).

Synthesis of [6,6′-μ-RS(1,7-$C_2B_9H_{10}$)$_2$-2-Co] (**2c–2h**). General Procedure

To a solution of the cesium salt [6,6′-μ-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co]Cs (0.1 g, 0.25 mmol) in propan-2-ol (5 ml), alkyl halide (propyl bromide, isopropyl bromide, allyl bromide, butyl bromide, hexyl bromide or ethyl iodide) (1 ml) was added and the reaction mixture was refluxed under nitrogen until the reaction was completed (TLC, benzene–hexane 1 : 2), *i.e.* for isopropyl-bridged compound **2e** 3 days, for propyl and ethyl derivatives 9 h, for other compounds 3.5 h. After evaporation of volatiles the product was extracted with benzene (3 × 5 ml), the solvent was distilled off in vacuum and the crude product was dissolved in hexane–dichloromethane (2 : 1) mixture (2 ml) and then filtered through SILICA-cart columns Separon SGX 60 μm (TESSEK, Prague, Czech Republic) using the same solvent mixture (3 ml) for elution. After evaporation of solvents, the product, orange-red powder, was recrystallized from pentane. Yield: **2c**, 53 mg (67%); **2d**, 67 mg (82%); **2e**, 31 mg (38%), **2f**, 72 mg (85%); **2g**, 71 mg (84%) and **2h**, 81 mg (90%).

TABLE IV
^{11}B NMR shifts δ, ppm, coupling constants *J*(B,H), Hz and ^{1}H {^{11}B} selectively decoupled chemical shifts δ_d, ppm of nitrogen bridged compounds **4**

Atoms	Compound								
	4a			**4b**			**4c**		
	δ	*J*	δ_d	δ	*J*	δ_d	δ	*J*	δ_d
B(12,12′)	–0.40	150	3.01	–0.84	144	2.98	–1.31	143	2.95
B(5,5′)	–3.56	155	3.02	–3.71	144	2.93	–3.94	155	2.87
				4.68	162	2.93			
B(6,6′)	–7.21[a]	–	–	–4.68[a]	–	–	1.81[a]	–	–
B(4,4′)	–11.00	165	3.21	–11.44	162	3.16	–11.59	165	3.15
B(9,9′)	–11.46	162	1.96	–11.44	162	1.95	–11.59	165	1.97
B(11,11′)	–12.96	156	2.07	–13.02	160	2.03	–14.42	159	2.13
				–14.50	165	2.09			
B(10,10′)	–16.59	147	1.87	–16.56	147	1.83	–17.28	147	1.90
				–17.53	161	1.89			
B(3,3′)	–18.60	164	1.88	–18.59	153	1.89	–18.57	155	1.93
B(8,8′)	–19.24	162	1.89	–19.28	160	1.87	–19.41	153	1.88

[a] Singlet.

[6,6′-μ-CH_3OCOCH_2S(1,7-$C_2B_9H_{10})_2$-2-Co] (**2i**)

To 0.19 M aqueous solution of [6,6′-μ-S(1,7-$C_2B_9H_{10})_2$-2-Co]Na (20 ml), Na_2CO_3 (2.0 g) was added followed by chloroacetic acid (1.0 g, 0.01 mol) and the mixture was heated to 60 °C. Formation of the respective acid was monitored by TLC of acidified samples (R_F 0.16, chloroform). After 6 h, although the starting species was still present, the reaction was interrupted, the solution was acidified, and the product was extracted with dichloromethane (2 × 10 ml) and filtered through a short silica gel column. The orange-yellow filtrate was evaporated to dryness, leaving 1.19 g (75%) of the TLC-pure [6,6′-μ-$HOCOCH_2$S(1,7-$C_2B_9H_{10})_2$-2-Co] acid. This compound was dissolved in methanol (20 ml) and $SOCl_2$ (0.5 ml) was added. The TLC spot of the acid gradually faded, being replaced by the spot of its methyl ester (R_F 0.70, chloroform). After standing overnight, the free acid disappeared completely. The solution was evaporated to dryness in vacuum, the residue was extracted with chloroform (2 × 10 ml), filtered through a short silica gel column, concentrated to 10 ml and hexane (30 ml) was carefully poured onto the chloroform solution avoiding mixing of both layers. After a week, deep orange prisms of **2i** separated (1.15 g, 70%).

[6,6′-μ-CH_3O(1,7-$C_2B_9H_{10})_2$-2-Co] (**3**)

To the 0.22 M aqueous solution of [(1,7-$C_2B_9H_{11})_2$-2-Co][H_3O] (10 ml), 28% aqueous formaldehyde solution (3 ml), concentrated hydrochloric acid (10 ml) and chloroform (15 ml) were added and the mixture was stirred under nitrogen for 24 h at ambient temperature. According to TLC monitoring no reaction took place. Stirring was continued for 3 h at 60 °C; the chloroform layer turned deep orange and a TLC spot with R_F 0.31 (benzene–hexane 1 : 2) appeared as the main product. The layers were separated, the chloroform layer was soaked into a dry silica gel column and the orange-yellow band was separated by elution with benzene–hexane (1 : 2). After evaporation to dryness in vacuum, the residue was recrystallized from hot hexane (20 ml); lustrous orange prisms (0.50 g, 64%) of the [6,6′-μ-CH_3O(1,7-$C_2B_9H_{10})_2$-2-Co] separated on standing overnight.

[6,6′-μ-H_2N(1,7-$C_2B_9H_{10})_2$-2-Co] (**4a**)

To a slurry of [(1,7-$C_2B_9H_{11})_2$Cs (2.303 g, 5.05 mmol) and $NaNO_2$ (0.8 g, 11.6 mmol) in benzene (25 ml) concentrated sulfuric acid (25 ml) was dropwise added under nitrogen and the reaction mixture was stirred for 3 days at ambient temperature. The benzene layer was separated and the aqueous layer was extracted with benzene (2 × 10 ml). Combined benzene extracts were evaporated to dryness, the resulting brown-red product was dissolved in CH_2Cl_2 (15 ml) and filtered through a silica gel column (TLC monitoring, benzene). Eluted fractions were evaporated and the product was recrystallized from hexane. Dark red crystals, yield 0.935 g (54%).

[6,6′-μ-MeHN(1,7-$C_2B_9H_{10})_2$-2-Co] (**4b**)

To a solution of the **4a** (0.150 g, 0.44 mmol) in 10% KOH (10 ml), 1 M solution of $(CH_3)_4NCl$ was added with stirring and the precipitated tetramethylammonium salt of **4b** was filtered off, washed with water (2 × 5 ml) and dried in vacuum. Yield 0.176 g (97%). To the slurry of this salt in benzene (20 ml), methyl iodide (2 ml) was added under nitrogen and the mixture was stirred at room temperature for 2 h. The resulting solution was filtered and evaporated to dryness. The crude product was purified by chromatography on silica gel (CH_2Cl_2). Recrystallization from hexane after stripping off CH_2Cl_2 from the eluate afforded dark red crystals, yield 0.107 g (68%).

[6,6′-μ-Me_2N(1,7-$C_2B_9H_{10}$)$_2$-2-Co] (**4c**)

To a solution of **4a** (0.107 g, 0.31 mmol) in 10% KOH (15 ml), an excess of dimethyl sulfate (1 ml) was added. The reaction mixture was stirred 5 min under nitrogen. Unreacted dimethyl sulfate was decomposed with aqueous ammonia (10 ml) and the product was extracted with benzene (3 × 10 ml). Combined benzene extracts were evaporated and the red-brown solid was purified by chromatography on a short silica gel column in hexane–dichloromethane (1 : 1) as eluent. The product was recrystallized from hexane. Dark red crystals, 0.108 g (94%).

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