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(Tetramethylcyclobutadiene)cobalt Complexes with Tricarbollide Ligands[‡]

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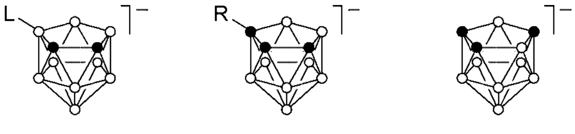
Reactions of the 11-vertex *nido*-tricarbollide anions $[7,8,9\text{-}C_3B_8H_{11}]^-$ (**2a**) and $[7,8,10\text{-}C_3B_8H_{11}]^-$ (**3**) with $[Cb^*Co(MeCN)_3]^+$ or $[Cb^*Co(C_6H_6)]^+$ ($Cb^* = C_4Me_4$) afford the expected cobaltatricarbollides $1\text{-}Cb^*\text{-}1,2,3,4\text{-}CoC_3B_8H_{11}$ (**4a**) and $1\text{-}Cb^*\text{-}1,2,3,5\text{-}CoC_3B_8H_{11}$ (**5**), respectively. A similar reaction of the amino-substituted anion $[7\text{-}t\text{BuNH-}7,8,9\text{-}C_3B_8H_{10}]^-$ (**2b**) is accompanied by polyhedral rearrangement even at room temperature, giving $1\text{-}Cb^*\text{-}12\text{-}t\text{BuNH-}1,2,4,12\text{-}CoC_3B_8H_{10}$ (**7b**). Complex **4a** rearranges to the isomeric complex **5** at 110 °C and further to $1\text{-}Cb^*\text{-}1,2,4,10\text{-}CoC_3B_8H_{11}$ (**6a**) at 160 °C. The amino-substituted derivative $1\text{-}Cb^*\text{-}10\text{-}t\text{BuNH-}1,2,4,10\text{-}CoC_3B_8H_{10}$ (**6b**) was obtained by isomerization of **7b** at 160 °C. The observed rearrangement sequence for $Cb^*CoC_3B_8H_{11}$ correlates well with the relative stabilities of nonmethylated analogs estimated by DFT calculations. The structures of **4a** and **7b** were determined by X-ray diffraction.

Introduction

Recently, we have developed two methods for the preparation of (tetramethylcyclobutadiene)cobalt complexes containing cyclopentadienyl, phospholyl, and pyrrolyl ligands, $Cb^*Co(C_4R_4E)$ ($Cb^* = C_4Me_4$; E = CR, P, and N).[2,3] One method is based on the reaction of the (carbonyl)iodide complex $Cb^*Co(CO)_2I$ with the corresponding anions, while another one uses the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ as a starting material. The second method is more general, allowing $Cb^*Co(C_4R_4E)$ compounds to be synthesized in higher yields under milder conditions. The same approaches proved to be useful in metallacarborane chemistry, which was clearly demonstrated by the synthesis of Cb*Co complexes with charge-compensated dicarbollide ligands $[9\text{-L-}7,8\text{-}C_2B_9H_{10}]^-$ (**1**).[1,4] The *nido*-tricarbollide anions **2** and **3**,[5] similar to **1**, have a five-membered face and a single negative charge, which makes them analogous to Cp^- in their coordinating ability. In contrast to dicarbollide derivatives, the presence of the third carbon atom hampers the prediction of the product structure owing to the ease of cluster rearrangement.[6–8] The chemistry of ferratricarbollides is well studied.[9] However, only one example of a cobalt derivative was described.[10] Herein we report the preparation of Cb*Co complexes of anions **2** and **3** and their further rearrangements.



L | R | 3
1a SMe$_2$ | 2a H |
1b NMe$_3$ | 2b NHBu^t |
1c py | |

○ BH ● CH

Results and Discussion

Synthesis and Rearrangements of Cobaltatricarbollides

We found that the room-temperature reaction of the tricarbollide anion $[7,8,9\text{-}C_3B_8H_{11}]^-$ (**2a**) with the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ in THF gives cobaltatricarbollide $1\text{-}Cb^*\text{-}1,2,3,4\text{-}CoC_3B_8H_{11}$ (**4a**)[11] (Scheme 1). The same compound was prepared by photochemical reaction of **2a** with the benzene complex $[Cb^*Co(C_6H_6)]^+$ in CH_2Cl_2.[12] The second method is more favorable as it avoids preliminary preparation of $[Cb^*Co(MeCN)_3]^+$ by irradiation of $[Cb^*Co(C_6H_6)]^+$ in MeCN.[13] As shown recently, the related iron complex $1\text{-Cp-}1,2,3,4\text{-}FeC_3B_8H_{11}$ is formed by a similar photochemical reaction of **2a** with $[CpFe(C_6H_6)]^+$.[8] The arrangement of the carbon atoms in the cobalt and iron complexes is the same as in the starting anion **2a**. In contrast, the room-temperature reaction of **2a** with $[Cp^*RuCl]_4$ is accompanied by polyhedral rearrangement to afford $1\text{-}Cp^*\text{-}1,2,3,5\text{-}RuC_3B_8H_{11}$,[8] indicating that the ease of the process depends on the nature of the metal.

[‡] (Tetramethylcyclobutadiene)cobalt Complexes, 4. Part 3: Ref.[1]

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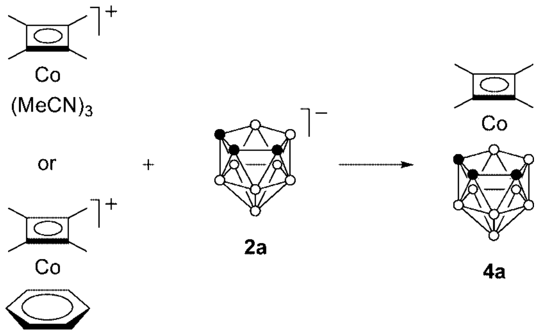
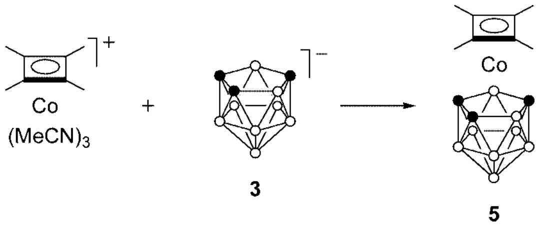


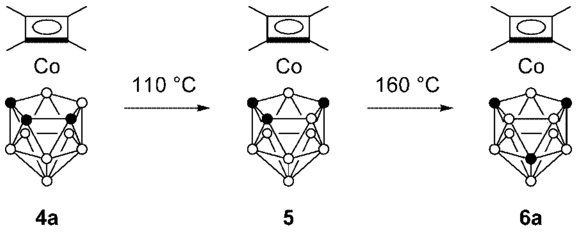
Scheme 1. Synthesis of cobaltatricarbollide **4a**.

The isomeric tricarbollide anion $[7,8,10\text{-}C_3B_8H_{11}]^-$ (**3**) reacts with $[Cb^*Co(MeCN)_3]^+$ to give cobaltatricarbollide 1-Cb*-1,2,3,5-$CoC_3B_8H_{11}$ (**5**) (Scheme 2). CpFe and Cp*Ru analogs have been prepared recently by reactions of **3** with $[CpFe(C_6H_6)]^+$ and $[Cp^*RuCl]_4$.[8] No rearrangement has been observed in these reactions.



Scheme 2. Synthesis of cobaltatricarbollide **5**.

Complex **4a** rapidly rearranges into **5** in refluxing toluene (Scheme 3). Refluxing of **4a** or **5** in diglyme results in selective formation of isomer 1-Cb*-1,2,4,10-$CoC_3B_8H_{11}$ (**6a**) with mutual *m*-disposition of cage carbon atoms. The same isomerization sequence was observed earlier for the iron and ruthenium analogs.[8] This sequence is associated with progressive space separation of the CH vertices and is consistent with a diamond-square-diamond mechanism.[14]



Scheme 3. Thermal rearrangements of **4a** and **5**.

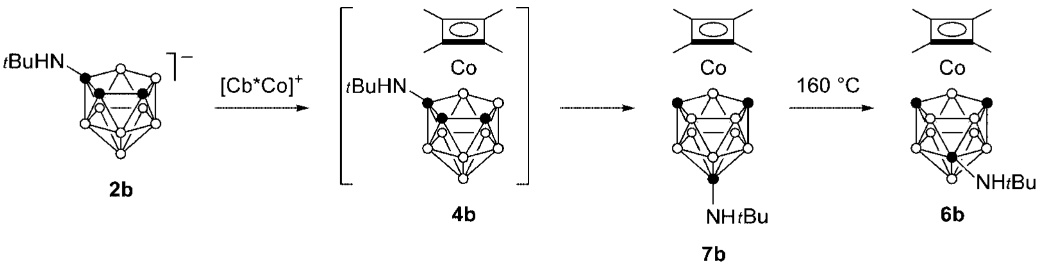
Unlike the parent anion **2a**, the room-temperature reaction of the amino-substituted derivative $[7\text{-}t\text{BuNH-}7,8,9\text{-}C_3B_8H_{10}]^-$ (**2b**) with $[Cb^*Co(MeCN)_3]^+$ (THF) or $[Cb^*Co(C_6H_6)]^+$ (CH_2Cl_2, *hν*) affords the rearranged *p*-substituted complex 1-Cb*-12-*t*BuNH-1,2,4,12-$CoC_3B_8H_{10}$ (**7b**) instead of the expected isomer 1-Cb*-2-*t*BuNH-1,2,3,4-$CoC_3B_8H_{10}$ (**4b**) (Scheme 4). Interestingly, treatment of **2b** with the less reactive (carbonyl)iodide complex $Cb^*Co(CO)_2I$ (THF, 65 °C) also gives **7b**, in contrast to an analogous reaction with **2a**, which does not lead to any isolable complexes. This suggests the higher nucleophilicity of **2b** compared with the parent anion **2a**, in accordance with a strong donor effect of the amino group. It should be added that reactions of anion **2b** with $CpFe(CO)_2I$ and $[Cp^*RuCl]_4$ also afford metallatricarbollides of the same cluster configuration.[7,15] Refluxing of the *p*-substituted compound **7b** in diglyme results in the formation of *m*-isomer 1-Cb*-10-*t*BuNH-1,2,4,10-$CoC_3B_8H_{10}$ (**6b**). Analogous transformation has been observed earlier for amino-substituted ferra- and ruthenatricarbollides.[7,16]

It can be concluded that the introduction of an amino substituent dramatically reduces the rearrangement barrier of the initial complexation product **4**.[17] Moreover, the substitution changes its rearrangement direction. Nevertheless, the final product has the same polyhedral structure in both cases (cf. Scheme 3 and Scheme 4).

X-ray Diffraction Study

Structures of the tricarbollide complexes **4a** and **7b** were confirmed by X-ray diffraction (Figure 1 and Figure 2). The Cb* ring is nearly an ideal square with a mean side length 1.453–1.457 Å, which approximates those found for the Cb*Co complexes with charge-compensated carborane ligands: 1.456 Å for Cb*Co[**1a**] and 1.452 Å for Cb*Co[**1c**].[1] The carbon atoms of the Cb* methyl groups are deviated for 0.10–0.20 Å from the ring plane away from the cobalt atom. The metal-bonding ligand planes are essentially coplanar, the dihedral angles being 1.2–2.9°.

The Co···Cb* distances in complexes **4a** (1.696 Å) and **7b** (1.703 Å) are slightly longer than that in Cb*Co(η-C_5H_4COMe) (1.683 Å)[3] but shorter than in Cb*Co[**1a**] (1.712 Å) and Cb*Co[**1c**] (1.711 Å),[1] suggesting that the tricarbollide ligands **2a** and $[1\text{-}t\text{BuNH-}1,7,9\text{-}C_3B_8H_{10}]^-$ are weaker donors than acetylcyclopentadienide but stronger donors than the charge-compensated dicarbollide ligands



Scheme 4. Synthesis and thermal rearrangement of **7b**.

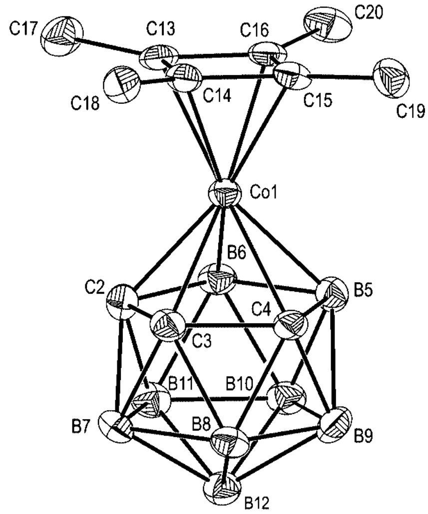


Figure 1. The molecular structure of 1-Cb*-1,2,3,4-$CoC_3B_8H_{11}$ (**4a**). Ellipsoids are shown at the 50% level. Selected bond lengths [Å] and angles [°]: Molecule 1: Co1–C2 2.052(3), Co1–C3 2.031(3), Co1–C4 2.051(3), Co1–B5 2.088(4), Co1–B6 2.092(4), C2–C3 1.595(4), C3–C4 1.596(4), C4–B5 1.702(5), B5–B6 1.780(5), C2–B6 1.684(5), B6–C2–C3 111.1(3), C2–C3–C4 109.7(2), C3–C4–B5 110.8(2), C4–B5–B6 103.8(3), B5–B6–C2 104.5(2). Molecule 2: Co1–C2 2.054(3), Co1–C3 2.035(3), Co1–C4 2.048(3), Co1–B5 2.096(4), Co1–B6 2.096(3), C2–C3 1.595(4), C3–C4 1.599(5), C4–B5 1.701(5), B5–B6 1.771(5), C2–B6 1.695(5), B6–C2–C3 110.9(3), C2–C3–C4 109.4(3), C3–C4–B5 111.2(2), C4–B5–B6 103.8(3), B5–B6–C2 104.7(3).

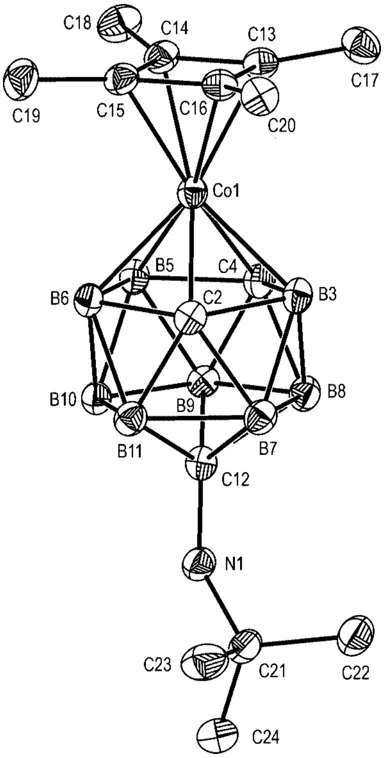


Figure 2. The molecular structure of 1-Cb*-12-*t*BuNH-1,2,4,12-$CoC_3B_8H_{10}$ (**7b**). Ellipsoids are shown at the 50% level. Selected bond lengths [Å] and angles [°]: Co1–C2 2.033(3), Co1–B3 2.028(3), Co1–C4 2.041(2), Co1–B5 2.058(3), Co1–B6 2.050(3), C2–B3 1.724(4), B3–C4 1.705(4), C4–B5 1.714(4), B5–B6 1.792(4), C2–B6 1.708(4), C12–B11 1.733(4), C12–B10 1.724(4), C12–B9 1.723(4), C12–B8 1.720(4), C12–B7 1.719(4), C12–N1 1.437(3); B5–B6–C2 104.86(19), B6–C2–B3 112.94(19), C2–B3–C4 103.19(19), B3–C4–B5 112.83(19), C4–B5–B6 105.5(2).

1a,**c**. However, according to electrochemical data, **1a**,**c** are stronger donors than tricarbollides.[18] Apparently, the Co···Cb* distance also depends on other effects.

DFT Calculations

Despite wide application of DFT calculations for transition-metal complexes,[19] their use in the case of metallacarboranes is rather limited.[20–24] Recently, we have shown that the calculations of ferratricarbollides $CpFeC_3B_8H_{11}$ provide reliable geometry, energy, and spectroscopic data.[8] In order to estimate the thermodynamic stability and ^{11}B NMR spectra of cobaltatricarbollides **4a**, **5**, and **6a**, we carried out DFT calculations (at the B3LYP/6-31G* level) for their nonmethylated analogs $(C_4H_4)CoC_3B_8H_{11}$ (**4a′**, **5′**, and **6a′**).[25]

The carbon-adjacent complex **4a′** was found to be the least thermodynamically stable, presumably because of the Coulomb repulsion of the negatively charged CH vertexes. The isomeric compounds **5′** and **6a′** are more stable than **4a′** for 17.2 and 26.2 kcal/mol, respectively. Thus, the observed rearrangement sequence **4a** → **5** → **6a** correlates with the stepwise increase of the thermodynamic stability of the isomers. Interestingly, the corresponding values for the CpFe analogs of **5′** and **6a′** are 17.0 and 25.5 kcal/mol, respectively, indicating that relative stability of isomers is mainly determined by the arrangement of the carbon atoms and is practically independent of the metal vertex.

The calculated ^{11}B NMR chemical shifts for **4a′**, **5′**, and **6a′** (Table 1) are in good agreement with the experimental values for **4a**, **5**, and **6a** (av. deviation 1.1 ppm), thus providing additional confirmation of their structures. The only significant deviation (about 3–5 ppm) is observed for the signal of the B12 atom, apparently because of approximation of the Cb* ligand with C_4H_4. Indeed, the calculation for the methylated complex **4a** decreases the deviation to 0.8 ppm. Such strong influence of the antipodal vertex on the ^{11}B NMR shift has been observed previously for various heteroboranes.[26]

Table 1. Calculated and experimental ^{11}B NMR chemical shifts of the $(C_4R_4)CoC_3B_8H_{11}$ isomers.

Compound	^{11}B NMR shifts				
	B5,6	B10	B9,11	B12	B7,8
4a exp.[a]	–9.6	–12.6	–17.1	–19.5	–26.1
4a′ calcd.	–9.7	–9.7	–16.5	–14.3	–27.6
4a calcd.	–9.9	–11.0	–17.1	–18.7	–27.7
	B12	B9,10	B7	B4,6	B8,11
5 exp.[a]	–16.6	–16.6	–16.6	–19.0	–24.6
5′ calcd.	–14.7	–15.5	–20.1	–17.0	–23.7
	B3	B5,6	B9,11	B12	B7,8
6a exp.[a]	–10.2	–11.1	–17.9	–19.0	–23.0
6a′ calcd.	–10.4	–12.0	–18.5	–17.0	–22.9

[a] In $CDCl_3$.

Conclusion

The methods previously used for the preparation of Cb*Co(C_4R_4E) compounds proved to be effective for the synthesis of Cb*Co complexes with monoanionic tricarbollide ligands. Similar to iron and ruthenium analogs, these complexes undergo cluster rearrangements in relatively mild conditions. Identical isomerization sequences observed for Cb*Co, CpFe, and Cp*Ru tricarbollides suggest that relative stability of isomers is mainly determined by the arrangement of the carbon atoms and is practically independent of the metal vertex. This conclusion is also confirmed by DFT calculations for (C_4H_4)Co and CpFe tricarbollide isomers.

Experimental Section

General: All reactions were carried out under argon in anhydrous solvents that were purified and dried using standard procedures. The isolation of products was conducted in air. Starting materials were prepared as described in the literature: Cb*Co(CO)$_2$I,[3,13] [Cb*Co(C_6H_6)]PF_6,[3,13] [Cb*Co(MeCN)$_3$]PF_6,[3,13] [Me_4N][**2a**],[5c] Tl[**2b**],[15] and [Ph_4P][**3**].[5c] Irradiation was conducted in a Schlenk tube using a high-pressure mercury vapor lamp with a phosphor-coated bulb (400 W). Both the tube and the lamp were placed in a vessel of an appropriate volume covered inside with aluminum foil; cooling was accomplished by running water. Column chromatography was performed on silica gel L 100/400 (0.5 × 10 cm) using CH_2Cl_2/petroleum ether (1:5) as an eluent. The ^{1}H and ^{11}B NMR spectra were recorded with a Bruker AMX 400 spectrometer operating at 400.13 and 128.38 MHz, respectively.

Preparation of 1-Cb*-12-*t*BuNH-1,2,4,12-Co$C_3B_8H_{10}$ (7b). Method A [Starting from Cb*Co(CO)$_2$I]: A mixture of Cb*Co(CO)$_2$I (100 mg, 0.29 mmol) and Tl[**2b**] (143 mg, 0.35 mmol) in THF (20 mL) was stirred under reflux for 13 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2/petroleum ether (1:1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (about 1 mL). Yield 90 mg (84%) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 1 H, NH), 1.52 (s, 12 H, Cb*), 1.50 (s, 2 H, CH), 1.25 (s, 9 H, *t*Bu) ppm. ^{11}B NMR: δ = –10.4 [d (148), 2B, B5,6], –15.1 [d (170), 1B, B3], –15.5 [d (160), 2B, B9,11], –17.9 [d (156), 1B, B10], –22.3 [d (173), 2B, B7,8] ppm. $C_{15}H_{32}B_8CoN$ (371.83): calcd. C 48.45, H 8.68, B 23.26, N 3.77; found C 48.63, H 8.74, B 23.30, N 3.59.

Method B {Starting from [Cb*Co(C_6H_6)]PF_6}: A mixture of [Cb*Co(C_6H_6)]PF_6 (50 mg, 0.13 mmol) and Tl[**2b**] (57 mg, 0.14 mmol) in CH_2Cl_2/THF (15:3 mL) was irradiated with stirring for 6 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2/petroleum ether (1:1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (about 0.5 mL). Yield 30 mg (62%).

Method C {Starting from [Cb*Co(MeCN)$_3$]PF_6}: Tl[**2b**] (102 mg, 0.25 mmol) was added to a frozen (–196 °C) solution of [Cb*Co(MeCN)$_3$]PF_6 (100 mg, 0.23 mmol) in THF (5 mL). The temperature was allowed to rise to ambient and the mixture was stirred overnight. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2/petroleum ether (1:1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (about 0.5 mL). Yield 68 mg (79%).

Preparation of 1-Cb*-1,2,3,4-Co$C_3B_8H_{11}$ (4a): Complex **4a** was obtained in a similar manner to **7b**, using [Me_4N][**2a**]. Yield 41% (method B) and 35% (method C) of a yellow solid. ^{1}H NMR ([D$_6$]acetone): δ = 4.53 (s, 1 H, CH), 2.77 (s, 2 H, CH), 1.68 (s, 12 H, Cb*) ppm. ^{11}B NMR: δ = –9.56 [d (148), 2B, B5,6], –12.72 [d (144), 1B, B10], –17.10 [d (158), 2B, B9,11], –19.03 [d (146), 1B, B12], –26.12 [d (170), 2B, B7,8] ppm. $C_{11}H_{23}B_8Co$ (300.70): calcd. C 43.93, H 7.71; found C 43.96, H 7.70.

Preparation of 1-Cb*-1,2,3,5-Co$C_3B_8H_{11}$ (5): Complex **5** was obtained in a similar manner to **7b**, using [Ph_4P][**3**]. Yield 61% (method C) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.50 (s, 2 H, CH), 1.91 (s, 1 H, CH), 1.60 (s, 12 H, Cb*) ppm. ^{11}B NMR: δ = –16.59 [d (159), 4B, B7,9,10,12], –18.99 [d (161), 2B, B4,6], –24.55 [d (159), 2B, B8,11] ppm. $C_{11}H_{23}B_8Co$ (300.70): calcd. C 43.93, H 7.71; found C 44.03, H 7.84.

Preparation of 1-Cb*-10-*t*BuNH-1,2,4,10-Co$C_3B_8H_{10}$ (6b): A solution of **7b** (50 mg, 0.13 mmol) in diglyme (3 mL) was refluxed for 6 h. The solvent was removed in vacuo, and the residue was dissolved in petroleum ether and filtered through a short layer of silica gel (about 2 cm). Evaporation left a yellow oil which crystallized at –10 °C. Yield 33 mg (66%) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 1.70 (s, 1 H, NH), 1.60 (s, 12 H, Cb*), 1.55 (s, 2 H, CH), 1.13 (s, 9 H, *t*Bu) ppm. ^{11}B NMR: δ = –8.4 [d (134), 2B, B5,6], –15.2 [d (156), 1B, B3], –16.0 [d (168), 2B, B9,11], –16.8 [d (190), 1B, B12], –24.7 [d (159), 2B, B7,8] ppm. $C_{15}H_{32}B_8CoN$ (371.83): calcd. C 48.45, H 8.68, B 23.26, N 3.77; found C 49.08, H 8.71, B 23.25, N 3.72.

Preparation of 1-Cb*-1,2,4,10-Co$C_3B_8H_{11}$ (6a): Complex **6a** was obtained in a similar manner to **6b** by refluxing a solution of **4a** or **5** (50 mg, 0.17 mmol) in diglyme (3 mL) for 13 h. Yield 35–38 mg (70–75%) of a yellow solid. ^{1}H NMR ([D$_6$]acetone): δ = 2.33 (s, 1 H, CH), 1.76 (s, 2 H, CH), 1.65 (s, 12 H, Cb*) ppm. ^{11}B NMR: δ = –10.15 [d (151), 1B, B3], –11.08 [d (155), 2B, B5,6], –17.90 [d (167), 2B, B9,11], –18.95 [d (161), 1B, B12], –23.03 [d (158), 2B, B7,8] ppm. $C_{11}H_{23}B_8Co$ (300.70): calcd. C 43.93, H 7.71, found C 44.05, H 7.82.

Computational Details: All calculations were performed using Gaussian 98 (revision A.7) software[27] at the B3LYP/6-31G* level. In the case of geometry optimization of **4a**, the methyl groups of the Cb* ring were fixed with ModRedundant option and treated with 3-21G* basis. The structures of the **4a′**, **5′**, and **6a′** isomers were optimized using tightened SCF convergence criteria (SCF = Tight option). The frequency calculations were performed to confirm the global minimum and include ZPE corrections to the energy. The ^{11}B NMR shifts were calculated using the GIAO method by subtraction of calculated isotropic shielding values from those of B_2H_6 (93.50 at B3LYP/6-31G*). The experimental chemical shift of B_2H_6 was assigned 16.6 ppm.[28]

X-ray Crystallography: Crystals of **4a** and **7b** suitable for X-ray diffraction were grown by slow evaporation of toluene solution under argon (**4a**) or by evaporation of petroleum ether solution in air (**7b**). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. All polyhedron hydrogen atoms were located from the Fourier density synthesis and refined in isotropic approximation. Crystal data and structure-refinement parameters for **4a** and **7b** are given in Table 2. All calculations were performed using the SHELXTL software.[29]

CCDC-279628 (for **4a**) and -279627 (for **7b**) contain the supplementary crystallographic data for this paper. These data can be

Table 2. Crystallographic data and structure-refinement parameters for **4a** and **7b**.

	4a	**7b**
Empirical formula	$C_{11}H_{23}B_8Co$	$C_{15}H_{32}B_8CoN$
Formula mass	300.70	371.83
Crystal color, habit	yellow prism	yellow prism
Crystal size [mm]	0.20 × 0.20 × 0.35	0.16 × 0.20 × 0.30
Diffractometer	Smart CCD	Smart CCD
Scan type	ω	ω
Temperature [K]	120	120
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	12.366(2)	8.746(1)
b [Å]	13.166(2)	18.540(3)
c [Å]	19.030(2)	12.750(2)
β [°]	92.730(3)	104.844(5)
V [Å^3]	3094.9(7)	1998.3(4)
Z [Z']	8 (2)	4(1)
$D_{\mathrm{calcd.}}$ [g/cm^3]	1.291	1.236
F (000)	1248	784
μ(Mo-K_α) [mm^{-3}]	10.87	8.56
θ range [°]	1.88–28.50	1.98–28.01
Collected reflections	18596	13672
Independent reflections (R_{int})	7571 (0.0674)	4660 (0.0394)
Observed reflections [$I > 2\sigma(I)$]	4328	3388
Parameters	457	354
R_1 (on F for obsd. refls.)[a]	0.0477	0.0472
wR_2 (on F^2 for all refls.)[b]	0.1026	0.1099
Gof	0.945	1.068
Largest diff. peak and hole [e/Å^3]	0.647/–0.351	0.456/–0.418

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$ for observed reflections. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections.

obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Contains details of DFT calculations for compounds **4a**, **4a′**, **5′**, and **6a′** (atomic coordinates for optimized geometry, energy data, summary of natural population analysis, and GIAO NMR shielding parameters).

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