



8,8'-μ-AMMONIUM DERIVATIVE OF COBALT BIS(DICARBOLLIDE) [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]

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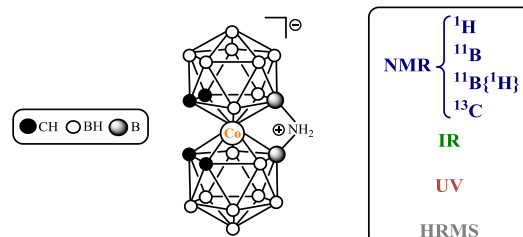
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Abstract

A zwitterionic *N*-bridged cobalt bis(dicarbollide) compound [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] was prepared by the reaction of [8,8'-μ-Et(HO)C=N-3,3'-Co(1,2-C₂B₉H₁₀)₂] with triethylamine in acetone. The complex obtained was characterized by NMR, IR, UV-Vis spectroscopy as well as high-resolution mass spectrometry.



Key words: cobalt bis(dicarbollides), sandwich complexes, monoatomic bridged compounds.

Introduction

The synthesis of a cobalt bis(dicarbollide) complex containing an NH₂-bridged group as a substituent [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] was first reported by Plešek *et al.* in 1976. The complex was prepared by the reaction of a cesium salt of cobalt bis(dicarbollide) Cs[3,3'-Co(1,2-C₂B₉H₁₁)₂] with nitrosulfuric acid in 47% yield [1]. Although the alkylation and acylation reactions of this complex were described in the literature, its characterization has never been reported [1–4].

In this work, we suggest a new method for obtaining [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] complex and present its characterization.

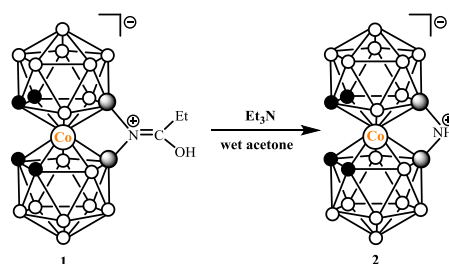
Results and discussion

It is known that the hydrolysis of 8-substituted nitrilium derivatives of transition metal bis(dicarbollide) complexes results in the formation of the corresponding iminols [5, 6]. The reaction of a propionitrilium derivative of cobalt bis(dicarbollide) furnishes [8-Et(HO)C=HN-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [6]. Recently, we have shown that the thermolysis of this complex leads to the formation of a number of intramolecular cyclization products, one of which is [8,8'-μ-Et(HO)C=N-3,3'-Co(1,2-C₂B₉H₁₀)₂] (**1**) bearing two dicarbollide ligands connected *via* a single-atom bridge [7]. Compound **1** is an *O*-protonated form of propionamide.

We found that the deprotonation of **1** with triethylamine leads to the cleavage of the double bond, resulting in the formation of [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (**2**) (Scheme 1).

Complex **2** was purified by column chromatography on silica gel using benzene as an eluent, which provided it in a high yield (84%).

The resulting complex was characterized by multinuclear NMR spectroscopy. The disappearance of the signals of the



Scheme 1. Reaction of [8,8'-μ-Et(HO)C=N-3,3'-Co(1,2-C₂B₉H₁₀)₂] with triethylamine.

ethyl group of **1** in the ¹H and ¹³C spectra of complex **2** was observed. The ¹¹B NMR spectrum contains five signals: a singlet from the substituted boron atom at 6.3 ppm and doublets at –0.9, –8.6, –15.6, and –24.1 ppm with the overall integral ratio of 2:2:8:4:2. It is worth noting that there was no splitting of the signals of the substituted boron atoms in the spectrum of **2**, which was observed in the case of amide **1**. In a similar way, there was no splitting of the signals of the carborane CH groups in the ¹H and ¹³C spectra of complex **2** (Table 1).

The ESI-HRMS spectrum of **2** showed a typical isotope distribution for B₁₈ compound with a peak of the maximum intensity at 337.2798 which corresponds to the proposed structure.

We assume that the reaction starts with the OH-proton abstraction by triethylamine. This results in the migration of the double bond from the nitrogen atom to the oxygen atom. This is facilitated by a decrease in the angle strain at the nitrogen atom. In complex **1**, the bridging nitrogen has sp²-hybridization with

Table 1. Selected signals in the NMR spectra of **1** and **2** (acetone-*d*₆, δ, ppm)

Comp.	CH _{carb}		8,8'-B
	¹ H	¹³ C	¹¹ B
1	3.92 and 3.95	46.8 and 47.2	5.5 and 6.5
2	3.94	47.0	6.3

an ideal angle for this type of hybridization being equal to 120°. At the same time, in complex **2**, the bridging nitrogen atom has sp³-hybridization with an ideal angle being equal to ~109°. According to the literature data, the B–N–B angle in the related amide is close to 98° [4], which indicates a strong angle strain in complex **1**. Thus, the transition of the nitrogen atom from sp²- to sp³-hybridization is highly favorable, since it reduces the angle strain. The migration of the double bond reduces the hydrolytic stability of the molecule. A similar effect is observed in organic amides containing nitrogen in a four-membered ring [8].

The hydrolysis is due to eventual water in acetone. It leads to highly basic amine [8,8'-HN-3,3'-Co(1,2-C₂B₉H₁₀)₂][−] which takes the proton from the Et₃NH⁺ moiety to form complex **2** (for the proposed mechanism of the reaction, see the Electronic supplementary information (ESI)).

Experimental section

[8,8'-μ-Et(HO)C=N-3,3'-Co(1,2-C₂B₉H₁₀)₂] was prepared according to the literature procedure [7]. Analytical grade acetone, benzene, and triethylamine were purchased from commercial sources and used without further purification. The reaction course was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% PdCl₂ in 1% HCl in aq. MeOH (1:10). Sigma-Aldrich silica gel (0.070–0.230 mm) was used for column chromatography. The NMR spectra were collected on a Varian Inova-400 spectrometer at 400.1 MHz (¹H), 128.4 MHz (¹¹B), and 100.0 MHz (¹³C). The signals in the ¹H and ¹³C NMR spectra were referenced to Me₄Si, whereas the signals in the ¹¹B NMR spectra were referenced to BF₃·Et₂O. All spectra were processed using the MestRenova software, version 6.0.2-5475. When processing ¹¹B and ¹¹B{¹H} NMR spectra, the baseline alignment was applied to improve the quality of integration. The IR spectra were recorded on an FSM-2201 (INFRASPEC) instrument. The UV-Vis spectra were recorded on an SF-2000 spectrophotometer (OKB SPECTR LLC) using 1 cm cuvettes. The high-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurement was made in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 mL·min^{−1}). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

Syntheses

Triethylamine (0.02 mL) was added to a solution of **1** (10 mg, 0.025 mmol) in acetone (1 mL). The resulting solution was stirred at room temperature for 1 min. The reaction mixture was evaporated to dryness under reduced pressure. The target product was isolated by column chromatography on silica using benzene as an eluent to give complex **2** as a red crystalline solid (7 mg, 84% yield).

¹H NMR (acetone-*d*₆): δ 3.94 (4H, s, CH_{carb}), 4.37–0.62 (16H, br. m, BH) ppm. ¹¹B NMR (acetone-*d*₆): δ 6.3 (2B, s), −0.9 (2B, d, *J* = 131 Hz), −8.6 (8B, d, *J* = 129 Hz), −15.6 (4B, d, *J* = 159 Hz), −24.1 (2B, d, *J* = 185 Hz) ppm. ¹³C NMR (acetone-*d*₆): δ 47.0 (CH_{carb}) ppm.

IR (film, cm^{−1}): 3050 (νNH), 2959 (νCH), 2935 (νCH), 2863 (νCH), 2580 (νBH), 1654 (δNH).

UV-Vis (acetone, nm): λ 330, 418, 497.

HRMS-ESI: *m/z* for C₄H₂₂B₁₈CoN: calcd. 337.2790 [M–H][−], obsd. 337.2798 [M–H][−].

Conclusions

A new method for the synthesis of [8,8'-μ-NH₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] was proposed. The title compound was characterized by multinuclear NMR spectroscopy and ESI-HRMS.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the NMR spectra of complex **2** and the proposed reaction mechanism. For ESI, see DOI: 10.32931/io2525a.

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