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8,8'-μ-Ammonium Derivative of Cobalt Bis(Dicarbollide) [8,8'-μ-NH2-3,3'-Co(1,2-C2B9H10)2]

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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).

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

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 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 pp 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).

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

|  |  |  |  |
| --- | --- | --- | --- |
| Comp. | CHcarb | | 8,8'-B |
| 1H | 13C | 11B |
| **1** | 3.92 and 3.95 | 46.8 and 47.2 | 5.5 and 6.5 |
| **2** | 3.94 | 47.0 | 6.3 |

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 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, CHcarb), 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 (CHcarb) 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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