



Reactions of bromine-bridged cobalt bis(1,2-dicarbollide) anion with arenes and nucleophiles



Irina Kosenko*, Irina Lobanova, Ivan Ananyev, Julia Laskova, Andrey Semioshkin, Vladimir Bregadze

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova Str. 28, 119991 Moscow, Russia

ARTICLE INFO

Article history:

Received 26 February 2016

Received in revised form

24 March 2016

Accepted 12 April 2016

Available online 27 May 2016

Keywords:

Cobalt bis(1,2-dicarbollide)

Bromonium bridged complex

Reactivity

X-ray structure

NMR spectroscopy

ABSTRACT

The generation of Br-bridged complex of cobalt bis(1,2-dicarbollide) ($8,8'-\mu\text{-Br-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$) and its reactions with arenes and some nucleophiles were studied. The complex $8,8'-\mu\text{-Br-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$ can be generated *in situ* via the action of 8-monobromo derivative of cobalt bis(1,2-dicarbollide) and AlX_3 ($\text{X} = \text{Cl, Br}$) in different aromatic solvents. This unstable complex was characterized by ^{11}B NMR spectroscopy for the first time. Its reactions with an appropriate arene led to $[\text{8-Br-}8'\text{-Ar-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ species even without addition of an activating Lewis base. Reactions of $8,8'-\mu\text{-Br-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$ with *S*- and *N*-nucleophiles (thioxane, morpholine) in benzene afforded the corresponding charge-compensated derivatives ($8\text{-Br-}8'\text{-Y-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$) as well as $[\text{8-Br-}8'\text{-Ar-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ species.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Functionalized derivatives of cobalt bis(1,2-dicarbollide)(-I) (COSAN, **1**, Fig. 1) are of increased interest for many aspects of fundamental [1,2] and applied chemistry [3].

Representative applications include extraction agents [4,5], HIV protease inhibitors [6], boron labels of DNA fragments [7] and many others [8–10]. Highly stable metallocarboranes $[\text{3,3}'\text{-M(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ ($\text{M} = \text{Fe, Co, Ni}$) are also known to be promising substrates for the preparation of molecular semiconductor materials [11,12]. Recently electroconductive properties of tetrathiafulvalenium salts of cobalt bis(1,2-dicarbollide)(-I) and its derivatives have been investigated [13–16]. Substituents in the boron cages in metallocarborane units play a crucial role in electroconductivity of these salts. Introduction of halogen substituents into the boron cage have improved electroconductivity of tetrathiafulvalenium salts of COSAN [17].

Bridged cobalt bis(1,2-dicarbollide)(-I) derivatives are prospective building-blocks for the preparation of various functionalized cobalt bis(1,2-dicarbollides)(-I) with different substituents in the boron cages. Thus, reactions of iodonium-bridged complex $8,8'-\mu\text{-I-}$

$3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$ (**2**, Fig. 1) with various nucleophiles (Nu) and arenes (Ar) have resulted in various 8, 8'- disubstituted species $[\text{8-I-}8'\text{-Nu-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]$ and $[\text{8-I-}8'\text{-Ar-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]$ respectively [18–23].

In contrast with compound **2**, until now a little has been known about the reactivity of $8,8'-\mu\text{-Br-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$ (**3**). Plešek et al. [23] have communicated the generation of this unstable complex *in situ* from $[(\text{8-Br-1,2-C}_2\text{B}_9\text{H}_{10})\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})]^-$ (**4**) and AlCl_3 in benzene. Its reactions with Me_2S and 1,4-dioxane have resulted in B-Br bridged bond cleavage leading to corresponding disubstituted species.

Herein we report reactions of generated *in situ* $8,8'-\mu\text{-Br-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2$ (**3**) with benzenes and nucleophiles and the synthesis of novel heterosubstituted derivatives of cobalt bis(1,2-dicarbollide).

2. Results and discussion

Recently we have reported an effective high-yield synthesis of iodonium-bridged derivative of COSAN **2** directly from cobalt bis(1,2-dicarbollide) (**1**), AlCl_3 and iodine [21]. However, our attempts to use this approach (using bromine) to prepare title complex **3** failed. Reaction of **1** with AlCl_3 in benzene led to a complex mixture of chlorinated derivatives of cobalt bis(1,2-dicarbollide). The replacement of AlCl_3 by AlBr_3 led to $8,8'$ -dibromo derivative of

* Corresponding author.

E-mail address: kosenko@ineos.ac.ru (I. Kosenko).

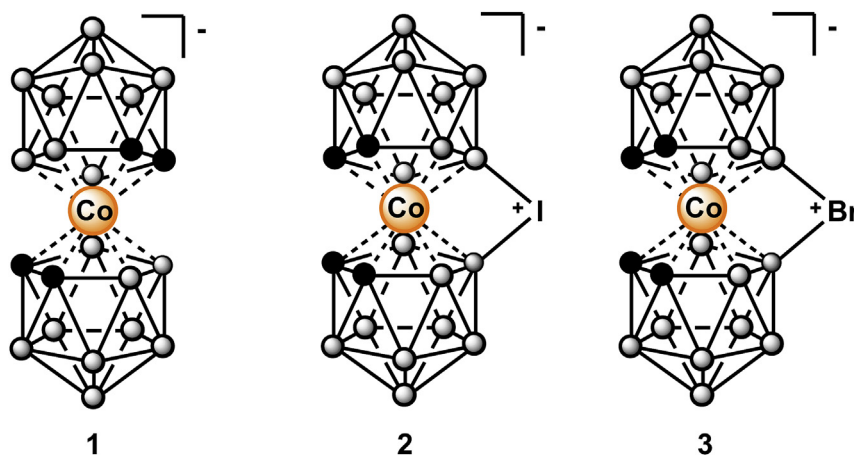


Fig. 1. COSAN (1), iodonium-bridged (2) and bromonium-bridged (3) complexes of COSAN.

cobalt bis(1,2-dicarbollide)(-1) as the main product.

Following the procedure of Plešek [23] we found that title bromonium complex **3** can be successfully generated *in situ* from Cs [4] in various aromatic solvents. Our modified procedure was as follows. Compound Cs[4] was refluxed in dry arene with an excess of AlCl_3 or AlBr_3 . The color of the orange suspension turned to red and formation of complex **3** was stated by TLC. Then a reaction mixture was passed through dry silica gel under argon to remove the rest of Cs[4] and inorganic materials. As a result, a solution of pure complex **3** in respective arene was obtained. Before our investigation, generation of **3** in benzene has been reported [23,24], but the only evidence of its existence was a TLC. We carried out reaction of Cs[4] and AlCl_3 in benzene/benzene- d_6 10/1 v/v as described above and characterized title compound **3** by $^{11}\text{B}\{^1\text{H}\}$ - and ^{11}B -NMR technique (Fig. 2).

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3** constituted of 4 signals with an intensity ratio of 4:8:4:2. This pattern is in agreement with structure of **3**. In the ^{11}B NMR spectrum of **3** a signal at $\delta = 2.3$ ppm split into a singlet at $\delta = 2.3$ ppm and a shoulder of a doublet at $\delta = 3.2$ ppm. Thus, a signal at $\delta = 2.3$ ppm can be definitely assigned as $\text{B}(8)\text{-Br}^+\text{-B}(8')$ of the complex **3**. This signal is shifted 5.6 ppm to the higher field compared to the signal of $\text{B}(8)\text{-Br}$ in the starting material Cs[4] [25]. The chemical shifts of BH groups in the ^{11}B -NMR spectrum of **3** were close to the data of iodonium bridged complex of COSAN **2** [23]. Our efforts to isolate compound **3** in solid state failed.

Treatment of a solution of **3** in benzene, generated from Cs[4] and AlBr_3 , with POEt_3 followed by 5 min reflux led to $[\text{8-Br-8}'\text{-C}_6\text{H}_5\text{-3,3}'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**5** $^-$). Then benzene was removed and the rest was treated by a saturated solution of CsCl_{aq} to precipitate rough Cs[5]. Purification by column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, 10/1 v/v) afforded pure Cs[5] with 7% yield (Scheme 1). The same entry, but generating **3** from Cs[4] with AlCl_3 in benzene, led to the same product Cs[5] with 26% yield. The conversion of **3** to **5** $^-$ proceeded within 5 h at the room temperature and without an addition of Lewis base. In this case Cs[5] of analytical purity was obtained by simple precipitation as Cs-salt, purification by column chromatography was not required. This experiment has indicated, that Br-bridged complex **3** seems to be more active towards benzene compared to I-bridged complex of COSAN **2**. Complex **2** has been inert towards benzene even at heating with UV-irradiation and its phenylation reaction has taken place only in the presence of a Lewis base [18].

Compound **5** $^-$ has been communicated previously [24], but not characterized. In the ^1H NMR spectrum of Cs[5] five signals were

observed. The phenyl group was represented by singlet at $\delta = 7.30$ and two doublets at $\delta = 7.18$ and 7.10 ppm. Signals of CH-groups of the dicarbollide ligands were detected at $\delta = 4.55$ and 3.73 ppm. In the ^{11}B -NMR spectrum of Cs[5] a pattern of 10 signals with an intensity ratio of 1:1:1:1:6:2:2:2:1:1 was observed. Two singlets at $\delta = 12.0$ and $\delta = 6.4$ ppm were assigned as $\text{B}(8')\text{-C}$ and $\text{B}(8)\text{-Br}$ respectively. In the ^{13}C NMR spectrum of Cs[5] signal of *ipso*-C-B(8') was observed as a characteristic broad signal at $\delta = 148.6$ ppm.

Generation of bromonium complex **3** from Cs[4] in toluene with AlBr_3 followed by a work up with POEt_3 and then with saturated solution of CsCl_{aq} resulted in 13% yield of 8-bromo-8'-tolyl derivative $[\text{8-Br-8}'\text{-CH}_3\text{C}_6\text{H}_4\text{-3,3}'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (Cs[6a,b]) (Scheme 1). This product was a mixture of *m*- (Cs[6a]) and *p*- (Cs[6b]) isomers in a ratio of 3:2 according to ^1H NMR spectrum. In the case of iodonium compound **2** all three possible *o*-, *m*- and *p*-isomers have been obtained in reaction with toluene in a ratio of 5:3:2 [18].

The reaction in toluene with AlCl_3 led to the isomers Cs[6a,b] in a same ratio of 3:2, however the yield was much higher (45%). This experiment was carried out at the room temperature, compound **3** was formed in 4 h, its complete conversion into Cs[6a,b] took additional 2 h and occurred without addition of POEt_3 .

In the ^1H NMR spectrum of Cs[6a,b] two doublets ($\delta = 7.18$, 6.99 ppm, both $J = 7.6$) corresponding to *p*-isomer were observed. A pattern consisting of a singlet at $\delta = 7.12$ ppm, a multiplet at $\delta = 7.07$ and a doublet at $\delta = 6.99$ ppm corresponded to *m*-isomer. The signals of two CH_3 -groups were detected at $\delta = 2.26$ ppm (*p*-isomer) and $\delta = 2.22$ ppm (*m*-isomer). A pattern in the ^{11}B -NMR spectrum of Cs[6a,b] was typical for 8-bromo-8'-aryl species (cf. experimental). In the ^{13}C NMR spectrum of Cs[6a,b] two broad signals at *ipso*-C atoms of both isomers were observed at $\delta = 148.5$ and 145.4 ppm.

These experiments demonstrated that bromonium complex of cobalt bis(dicarbollide) **3** can be generated from 8-monobromo derivative Cs[4] *in situ* and then arylated by aromatic solvent used. Optional conditions for the preparation of **3** include carrying out a reaction of Cs[4] with AlCl_3 . Perhaps, the use an excess of more active AlBr_3 increases decomposition of **3**. As a result, dramatic decrease of the yields of complex **3** took place according to the yields of $[\text{8-Br-8}'\text{-Ar-3,3}'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ calculated from starting Cs[4].

Indeed, generation of the complex **3** from Cs[4] in *o*-xylene with AlCl_3 followed by treatment with POEt_3 resulted in 28% isolated yield of a single isomer $[\text{8-Br-8}'\text{-(3,4-(CH}_3)_2\text{C}_6\text{H}_4)\text{-3,3}'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (Cs[7]) (Scheme 1). In contrast, the same entry but

Download English Version:

<https://daneshyari.com/en/article/1321669>

Download Persian Version:

<https://daneshyari.com/article/1321669>

[Daneshyari.com](https://daneshyari.com)