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Fluorination studies of the [commo-3,3′-Co(3,1,2-$CoC_2B_9H_{11})_2^{-1}$] ion

Alexander N. Gashti [a], John C. Huffman [a], Aaron Edwards [a], Gabriella Szekeley [b], Allen R. Siedle [b], Jonathan A. Karty [a], James P. Reilly [a], Lee J. Todd [a],*

[a] *Department of Chemistry, and Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102, USA*
[b] *3M Corporate Research Laboratories, Science Research Laboratory, 3M Company, 3M Center, Building 201-2S-05, St Paul, MN 55144-1000, USA*

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Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday.

Abstract

Reactions of the cobalt bis(dicarbollide) anion [commo-3,3′-Co(3,1,2-$CoC_2B_9H_{11})_2^{-1}$] with the mild fluorinating agent, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA) in anhydrous acetone were studied. Synthetic methodologies as well as ^{11}B-, ^{19}F-NMR, and negative ion elecrospray mass spectrometric (NIEMS) characterization of the 8,8′ difluoro derivative of this anion [commo-3,3′-Co(8-F-3,1,2-$CoC_2B_9H_{10})_2^{-1}$] are reported here. The structure of NBu_4 salt of the 8,8′ difluoro derivative was determined by single crystal X-ray crystallography. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Sandwich compounds; Boron; Carborane; Fluorination; Cobalt bis(dicarbollide) anion

1. Introduction

Halogenation of monoanionic carboranes has recently received much attention because of their potential use as weakly coordinating anions. The cobalt bis(dicarbollide) anion (**1**) is one of the most widely studied monoanionic, carborane, 'sandwich' complexes, and several studies concerning its halogenation have been reported [1]. Treatment of **1** with elemental iodine in methanol affords either the monoiodo derivative [commo-3,3′-Co(8-I-3,1,2-$CoC_2B_9H_{10}$)(3,1,2-$CoC_2B_9H_{11})^{-1}$] or diiodo derivative [commo-3,3′-Co(8-I-3,1,2-$CoC_2B_9H_{10})_2^{-1}$] [1]. The hexaiodo derivative [commo-3,3′-Co(8,9,12-I_3-3,1,2-$CoC_2B_9H_8)_2^{-1}$] has been synthesized via the reaction of **1** with iodine monochloride in refluxing dichloromethane [1]. The 8,8′ dibromo derivative of **1** has been prepared via *N*-bromosuccinimide in refluxing tetrahydrofuran [2], and the reaction of **1** with elemental bromine in refluxing glacial acetic acid affords the hexabromo derivative [commo-3,3′-Co(8,9,12-Br_3-3,1,2-$CoC_2B_9H_8)_2^{-1}$] [3]. The 8,8′ dichloro derivative of **1** has been prepared with *N*-chlorosuccinimide in refluxing tetrahydrofuran or by acidified sodium hypochlorite (HCl–NaOCl) [2].

Until recently the fluorination of **1** has not been achieved. As first noted by Ivanov et. al. [4] treatment of the cesium salts $CB_{11}H_{12}^{-1}$, $CB_9H_{10}^{-1}$, $B_{12}H_{12}^{-2}$, and $B_{10}H_{10}^{-2}$ with F-TEDA results in the fluorination of specific B–H vertices. We herein describe the fluorination of **1** using F-TEDA to obtain **2** (Fig. 1) and other fluorinated derivatives.

2. Experimental

2.1. General comments

Schlenk, high-vacuum techniques were used with dry nitrogen when an inert environment became necessary. The sodium salt of **1** was obtained from Strem Chemicals, Newburyport, MA. Solvents used were reagent

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* Corresponding author. Tel.: +1-812-8558733; fax: +1-812-8558300.
E-mail address: toddlj@indiana.edu (L.J. Todd).

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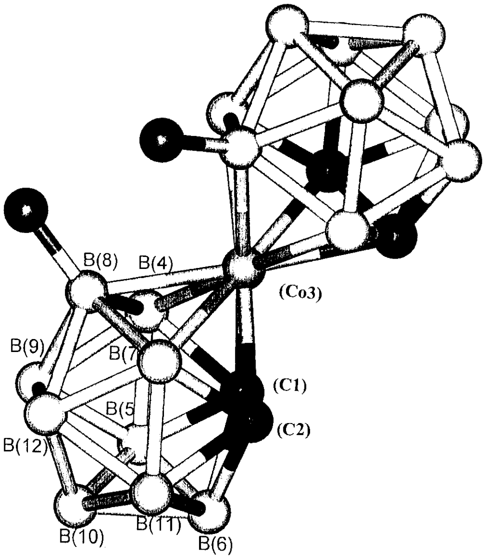

Fig. 1.

grade. F-TEDA was purchased from Aldrich Chemical Co. and was used as received. ^{11}B- and ^{19}F-NMR spectra were recorded at 128.4 and 376.4 MHz, respectively, using an INOVA 400 spectrometer. Boron chemical shifts were measured at 0 ppm relative to an external reference $BF_3 \cdot O(C_2H_5)_2$. Fluorine chemical shifts were measured at -77.25 ppm relative to an external reference of CF_3CO_2H in C_6D_6. Solid samples for NIEMS were dissolved in a 1:1 mixture of 1 mM ammonium acetate buffer (pH 7) and acetonitrile. Mass spectra were obtained at 3M Co. using a Zabspec magnetic sector mass spectrometer and at Indiana University using a Finnegan TSQ electrospray mass spectrometer.

2.2. Synthesis of *$NBu_4[commo$-3,3′-$Co(8$-F-3,1,2-$CoC_2B_9H_{10})_2^{-\,1}]$* (**2**)

A mixture of the NBu_4^+ salt of **1** (0.8 g, 1.76 mmol) and the F-TEDA (5.6 g, 15.8 mmol) was stirred in dry acetone at 50°C under a dry nitrogen atmosphere for 100 h. Upon completion of the reaction, an orange solution was filtered. Being sparingly soluble in acetone, most of the residual F-TEDA remained as a white solid precipitate, while the orange liquid was collected as a filtrate. The solvent was evaporated in vacuo, and orange crystals were then grown by slow evaporation from a saturated solution of ethanol and water. ^{11}B-NMR data are summarized in Table 1. ^{19}F-NMR data is shown in Table 2 and is compared to other fluorinated anionic carboranes. The NIEMS spectrum of the crystals indicates that the following anions were present: **2** being the major product (79.6%), monofluoro (**3**) (10.3%), and trifluoro (**4**) (10.1%) derivatives. The approximate percentage for each component was computed by summing the area for all of the peaks in each compounds isotopic envelope and dividing it by the total area for all three products.

Table 2
^{19}F-NMR (acetone-d_6) for compound **2** and other fluorinated boranes

Compound	δ-values	Reference
NBu_4(**2**)	−144 (B8, B8′)	This work
(12-$CB_{11}H_{11}F^-$)	−190.4 (B12)	[4]
($7,12$-$CB_{11}H_{10}F_2^-$)	−194.4 (B12), −212.0 (B7)	[4]
($7,9,12$-$CB_{11}H_9F_3^-$)	−198.1 (B12), −216.0 (B7, B9)	[4]

2.3. X-ray structural characterization

The details of the crystallographic experiment and subsequent computations are summarized in Table 3. A typical crystal mounted on a glass fiber using silicone grease and placed on the diffractometer where it was cooled to −176°C. The crystals are thermochromic, changing from orange to yellow upon cooling. A systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed monoclinic symmetry with systematic absences corresponding to the space group $P2_1/m$ or $P2_1$. Subsequent solution and refinement confirmed the non-centrosymmetric choice, $P2_1$. The data were collected using a standard moving crystal-moving detector technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent reflections were averaged. The structure was solved using direct methods (MULTAN) and Fourier techniques. Most hydrogen atoms were visible in a difference Fourier synthesis phased on the non-hydrogen atoms and all hydrogens were included as fixed isotropic contributors in the final cycles of refinement. A final difference Fourier was featureless

Table 1
^{11}B-NMR (acetone-d^6) for compound **2**

Compound	B8	B10	B9, B12	B4, B7	B5, B11	B6
NBu_4(**2**) δ-values, multiplicity	+28.02 s	−3.17 d	−5.68 d	−8.07 d	−19.57 d	−29.13 d
Coupling constants	^1J(BF) 78.14	^1J(BH) 148.63	^1J(BH) 142.52	^1J(BH) 148.02	^1J(BH) 156.56	^1J(BH) 166.01
Na(**1**) δ-values, multiplicity	+6.8 d	+1.6 d	−5.0 d	−6.0 d	−17.0 d	−22.5 d

Table 3
Crysrallographic data for [commo-3,3′-Co(8-F-3,1,2-CoC$_2$B$_9$H$_{10}$)$_2^{-1}$]

Empirical formula	$C_4H_{20}B_{18}CoF_2^-$; $C_{16}H_{36}N^+$
Formula weight	620.20
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	16.151(2)
b (Å)	11.979(2)
c (Å)	18.466(3)
α (°)	90
β (°)	109.19
γ (°)	90
V (Å^3)	3374.25
D_{calc} (g cm^{-3})	1.185
Z	4
F(000)	1272
Crystal size (mm^3)	0.40 × 0.40 × 0.30
λ(Mo–K$_\alpha$) (Å)	0.71069
μ (cm^{-1})	5.356
T (K)	97.15
Reflections collected	11030
Detector-sample distance (cm)	22.5
Sample source-distance (cm)	23.5
Take off angle (°)	2.0
Average ω–scan width at half-height (°)	0.25
Scan speed (° min^{-1})	4.0
Scan width (°)	2.0 + dispersion
Single background time-extremes of scan (s)	6
Aperture size (mm)	3.0 × 4.0
Collection limit (2θ) (°)	6–50
Unique intensities	6225
$F > 0.0$	6225
$F > 2.33\sigma(F)$	3713
R for averaging	0.036
Final residuals	
$R(F)$[a]	0.0873
$R_w(F)$[b]	0.0817
Goodness-of-fit for last cycle	2.376
Max. δ/σ for last	0.008

with the largest peak of intensity 1.40 e A^{-3} adjacent to one of the Cobalt atoms.

3. Results and discussion

3.1. Synthesis

A range of synthetic routes has been used for the halogenation of monoanionic carboranes. Earlier studies have shown that F-TEDA induces a higher degree of fluorination than anhydrous HF making it highly effective for B–H → B–F transformations [5]. The reaction of the NBu$_4$ (**1**) with 15 equivalents of F-TEDA in anhydrous acetone at 50°C followed by fractional crystallization results in the formation of three new compounds. The characterization of salts of **2**, **3**, and **4** included ^{11}B- and ^{19}F-NMR as well as a negative ion electrospray mass spectrum (NIEMS). By changing the reaction conditions more highly fluorinated derivatives have been obtained, up to the heptafluoro derivative, as evidenced by negative ion electrospray mass spectra. These will be reported at a later date.

^{11}B spectra for the NBu$_4$ (**2**) exhibit a total of six resonances consistent with the structure and symmetry of this anion. The intensity pattern is as follows: 1:1:2:2:2:1, reading from low to high magnetic field. ^{11}B-^{1}H coupling occurs at five of the six resonances believed to be the B10 position, B9, B12 equivalence, B4, B7 equivalence, B5, B11 equivalence, and B6 position. Due to the presence of the electron-withdrawing substitutent, the boron atoms at the fluorinated B8, B8′ positions are expected to exhibit a significant downfield signal relative to the B8, B8′ position of **1**. ^{19}F-NMR (Table 2) exhibits a single quartet representing the fluorine atoms on the B8, B8′ positions. The chemical shift $\delta = -144$, is compared with other fluorine-substituted carboranes [4]. Furthermore, this ^{19}F-signal was decoupled in the one-dimensional ^{11}B-NMR spectrum, and the boron signal for the B8, B8′ position became significantly sharper relative to the uncoupled ^{11}B-spectrum. This strongly suggests B–F coupling is occurring at the most downfield resonance in the one-dimensional ^{11}B spectrum. The one-dimensional ^{11}B-spectrum also contains very small doublets at $\delta = 7.13$, 1.72, and -16.67. These are believed to be the B8, B10, and B5, B11 positions of the unsubstituted dicarbollide ligand of **3** when the chemical shifts are compared with the starting material, **1** (Table 1). Because compound **4** is probably not very symmetrical and is also a very minute product from NIEMS, we are unable to report its ^{11}B-NMR data.

The two-dimensional ^{11}B–^{11}B COSY NMR spectrum (Fig. 2) illustrate that the doublet near $\delta = -8.01$, representative of the B4, B7 positions, couples with the singlet near $\delta = 28.06$, due to the fluorinated B8, B8′ position. This singlet weakly couples with the doublet centered at $\delta = -5.72$, representing the B9, B12 positions. The doublet, corresponding to the B9, B12 positions couples with the doublet at around $\delta = -19.48$, due to the B5, B11 positions, that is also coupled to the doublet near $\delta = -3.15$, believed to be the B10 position. From these data, peak assignments were inferred for the one-dimensional ^{11}B spectrum (Table 1).

Fig. 3 illustrates observed NIEMS spectrum of NBu$_4$(**2**). The peak distribution is broad, due to the isotopic pattern of boron having 80% ^{11}B and 20% ^{10}B. The parent ion set of peaks is found at m/z 356–363. These data are consistent for a monoanion with 18 boron atoms, four carbon atoms, 20 hydrogen atoms, one cobalt atom, and two fluorine atoms. Notice the two small peaks to the left and right of the major peak, believed to represent minor products **3** and **4** observed around m/z 341 and around m/z 377, respectively. As first noted by Gaines et al. [6], when evaluating the

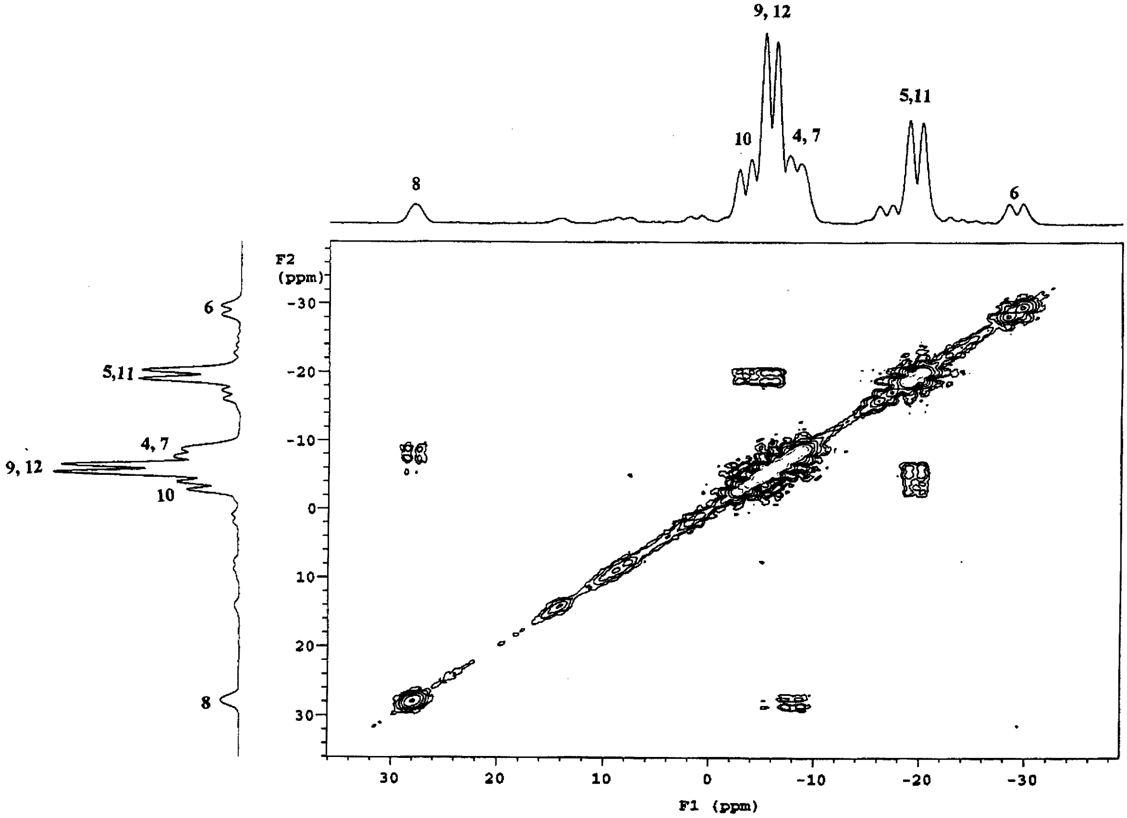

Fig. 2. Two-dimensional ^{11}B–^{11}B COSY spectrum.

composition of polyhedral borane salts, NIEMS becomes a very sensitive technique.

3.2. *X-ray structure analysis*

The structure of **2** is shown in Fig. 1. Selected bond angles and distances are given in Tables 4 and 5. This anion consists of two $C_2B_9H_{11}^{-2}$ (dicarbollide) units sandwiched around a formal Co^{3+} ion with monoclinic symmetry. Fluorine substituents are designated on the cluster vertices at the B8 and B8′ boron atoms. The B8–F8 bond distance of **2** (1.428 (14) Å) is not substantially different when compared with the boron–fluorine bond distance observed in the monoanion [6,7,8,9-$CB_9H_5F_4$-10-$NHCOCH_3^{-1}$] (1.376 (9)–1.385 (9) Å) [5] or the dianion [$CuCl(CB_{11}F_{11})^{-2}$] (1.367 (7)–1.383 (6) Å) [7]. When compared with the X-ray structure of the **1**, the B9–B8–F8 bond angle of **2** (115 (10)°) is not significantly different from the B9–B8–H8 bond angle (121.21 (1)°) [8]. Similarly, B12–B8–H8 bond angle of **1** (120.62° (2)) does not vary considerably with that of the B12–B8–F8 bond angle of **2** (116.3° (10)).

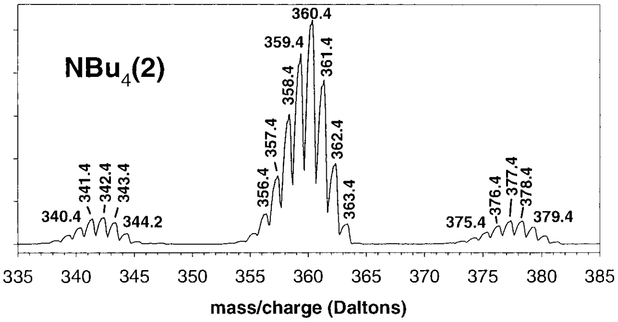

Fig. 3. Negative ion electrospray mass spectrum of NBu_4 (**2**).

Table 4
Selected bond distances (Å) for compound **2**

Bond distance			
Co3–B4	2.132 (15)	B8–F8	1.428 (14)
Co3–B8	2.145 (13)	B8–B7	1.770 (17)
Co3–B7	2.121 (11)	B8–B9	1.795 (17)
Co3–C1	2.024 (10)	B8–B12	1.753 (18)
Co3–C2	2.059 (10)	B8–B4	1.800 (19)

Table 5
Selected bond angles (°) for compound **2**

Angle	A	B	C
64.8 (6)	Co3	B8	B7
64.7 (6)	Co3	B8	B4
59.7 (7)	B7	B8	B12
59.8 (7)	B12	B8	B9
59.0 (7)	B4	B8	B9
117.8 (8)	Co3	B8	F8
125.7 (9)	F8	B8	B7
116.3 (10)	F8	B8	B12
115.0 (10)	F8	B8	B9
123.5 (10)	F8	B8	B4

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148465. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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