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Synthesis, structure and properties of mixed-sandwich cobalta- and ferra-carboranes with ‘carbon-atoms-adjacent’ C_2B_9 and C_2B_{10} systems ☆

Zaozao Qiu, Kit-Hung Wong, Zuowei Xie*

Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

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ABSTRACT

Several ‘carbon-atoms-adjacent’ mixed sandwich cobalta- and ferra-carboranes incorporating the C_2B_{10} and C_2B_9 systems were synthesized via salt metathesis reactions followed by the oxidation with oxygen, which included unexpected cobaltacarboranes $[(\eta^5\text{-}C_5H_5)\{\eta^6\text{-}[C_6H_4(CO)(CH_2)]C_2B_{10}H_{10}\}]Co$ and $[(\eta^5\text{-}C_5H_5)\{\eta^6\text{-}[C_6H_4(CHOH)(CH_2)]C_2B_{10}H_{10}\}]Co$. All new metallacarboranes were characterized by various spectroscopic techniques, elemental analyses and single-crystal X-ray diffraction studies. The electrochemical data suggest that cyclopentadienyl is the most electron-rich ligand followed by the C_2B_9 and then C_2B_{10} systems, and ‘carbon-atoms-adjacent’ C_2B_{10} system is more electron-donating than its ‘carbon-atoms-apart’ counterpart.

1. Introduction

o-Carborane (*o*-$C_2B_{10}H_{12}$) can be converted to the *nido*-$C_2B_9H_{11}^{2-}$ [1], ‘carbon-atoms-apart’ (CAp) *nido*-7,9-$C_2B_{10}H_{12}^{2-}$ [2] and *arachno*-$C_2B_{10}H_{12}^{4-}$ [3]. If the two cage carbon atoms are linked by a short linkage, the corresponding ‘carbon-atoms-adjacent’ (CAd) *nido*-$R_2C_2B_9H_9^{2-}$ [4], *nido*-7,8-$R_2C_2B_{10}H_{10}^{2-}$ [5] and *arachno*-$R_2C_2B_{10}H_{10}^{4-}$ [6] are then generated. These anions are good π ligands for transition metals, leading to the formation of a large class of metallacarboranes [7]. The CAd anions are also finding applications in the synthesis of supercarboranes, whereas the CAp isomers are not appropriate starting materials for this purpose [8]. These results suggest that CAp and CAd isomers have their own uniqueness in “polyhedral expansion” processes. In view of the well established chemistry of CAp metallacarboranes, d-block transition metal metallacarboranes bearing CAd C_2B_{10} systems are largely unexplored [9]. In this connection, we extended our research to include CAd cobalta- and ferra-carboranes with the aim to directly compare the properties of both CAd and CAp metallacarboranes, which in turn may enhance our understanding of the electronic properties of the CAd and CAp ligands. We report herein the synthesis, structure and properties of mixed sandwich cobalta- and ferra-carboranes incorporating 7,8-[*o*-$C_6H_4(CH_2)_2$]-7,8-$C_2B_9H_9^{2-}$ and 7,8-[*o*-$C_6H_4(CH_2)_2$]-7,8-$C_2B_{10}H_{10}^{2-}$ ligands.

2. Results and discussion

2.1. Synthesis

Salt metathesis is a general method for the production of metallacarboranes. Reaction of anhydrous $CoCl_2$ with $[\{\mu\text{-}7,8\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}7,8\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$ (**1**) [5b] and CpNa ($Cp = C_5H_5$) in THF at temperature range −78 to 0 °C followed by oxidation with O_2 afforded, after column chromatographic separation, a major product $[(\eta^5\text{-}C_5H_5)\{\eta^6\text{-}[C_6H_4(CH_2)_2]C_2B_{10}H_{10}\}]Co$ (**2a**) (36%), and three minor products, $[(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}[C_6H_4(CH_2)_2]C_2B_9H_9\}]Co$ (**3**) (6%), $[(\eta^5\text{-}C_5H_5)\{\eta^6\text{-}[C_6H_4(CO)(CH_2)]C_2B_{10}H_{10}\}]Co$ (**4**) (2%), and $[(\eta^5\text{-}C_5H_5)\{\eta^6\text{-}[C_6H_4(CHOH)(CH_2)]C_2B_{10}H_{10}\}]Co$ (**5**) (2%) (Scheme 1). Recrystallization of **2a** from THF at room temperature gave its isomer **2b** with a different orientation of the $C_6H_4(CH_2)_2$ unit in the solid-state structure.

The isolation of **4** and **5** were unexpected, which may be ascribed to the formation of peroxide in the presence of excess O_2 and $CoCl_2$ in THF [10]. The activated O_2 by $CoCl_2$ may insert the C—H bond of the methylene unit to form peroxide, which eventually turns into the hydroxyl and carbonyl group in the side wing.

On the other hand, the presence of excess CpNa and the hydroxide ion resulted from the above mentioned peroxide may be responsible for the formation of the deboration product **3**. It is assumed that the strong base attacks one of the cage boron atoms on the C_2B_4 bonding face of **2** to give $[(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}[C_6H_4(CH_2)_2]C_2B_9H_9\}]Co$ (**3**). Similar reactions were previously observed. For examples, $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_{11})]Co$ and $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})]$

☆ Dedicated to Professor Thomas Fehlner on the occasion of his 75th birthday.

* Corresponding author. Fax: +86 852 26035057.
E-mail address: zxie@cuhk.edu.hk (Z. Xie).

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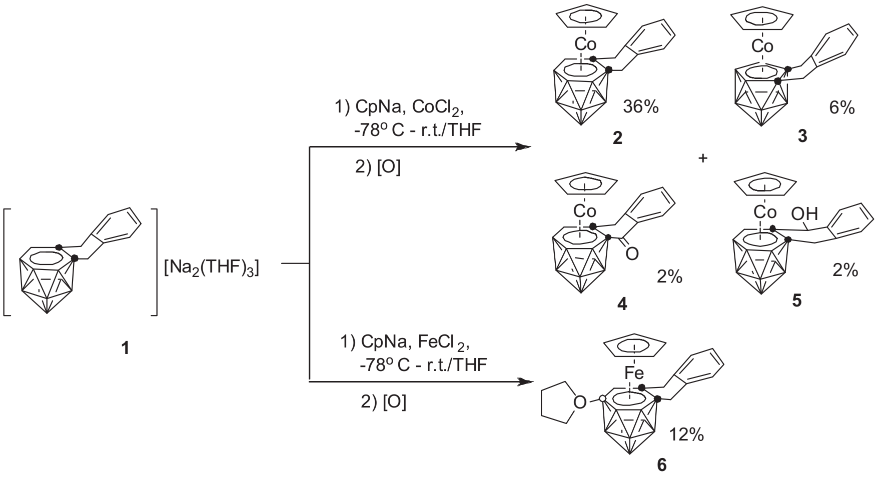


Scheme 1. Synthesis of cobalta- and ferra-carboranes with C_2B_{10} system.

Co were obtained as the by-products in the synthesis of [(η^5-C_5H_5)(η^6-$C_2B_{10}H_{12}$)]Co and [(η^5-C_5Me_5)(η^6-$C_2B_{10}H_{12}$)]Co, respectively [2,11].

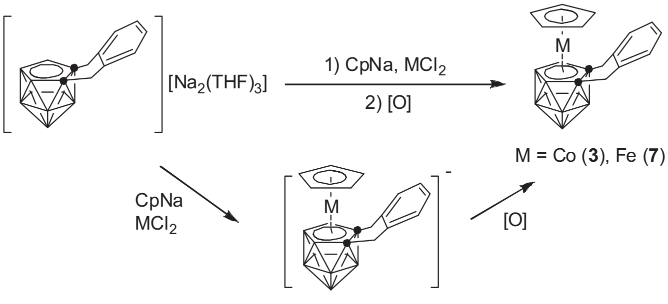
In a similar manner, treatment of anhydrous $FeCl_2$ with **1** and CpNa in THF gave, after oxidation with O_2 and column chromatographic separation, a zwitterionic salt [(η^5-C_5H_5){η^6-[$C_6H_4(CH_2)_2$]-4-(THF)-$C_2B_{10}H_9$}]Fe (**6**) in 12% yield and other unidentified paramagnetic species (Scheme 1). It was noted that no pure products were isolated without oxidation by O_2. Complex **6** is a diamagnetic 18-electron Fe(II) complex. A THF molecule was introduced to the cage boron atom of the C_2B_4 face, allowing the isolation of a relatively air- and moisture-stable divalent 18-electron ferracarborane. It has been documented that the boron atom at the open face of carborane cage can be attacked by electrophiles to generate oxonium species [12]. The isolation of **6** may imply that the nucleophile could attack the B(4) position of the C_2B_4 bonding face, leading to the formation of deboration product such as **3**.

The deboration products [(η^5-C_5H_5){η^5-[$C_6H_4(CH_2)_2$]$C_2B_9H_9$}]Co (**3**) and [(η^5-C_5H_5){η^5-[$C_6H_4(CH_2)_2$]$C_2B_9H_9$}]Fe (**7**) were prepared by salt metathesis reaction of MCl_2 (M = Co or Fe) with {η^5-[$C_6H_4(CH_2)_2$]$C_2B_9H_9$}$Na_2(THF)_3$ [9b] in THF followed by oxidation with O_2 in 64% and 43% yield, respectively, as shown in Scheme 2.

Complexes **2**, **4**, **5** and **6** are soluble in CH_2Cl_2, THF, acetone and MeCN, slightly soluble in toluene and $CHCl_3$ but insoluble in *n*-hexane, whereas **3** and **7** are soluble toluene, $CHCl_3$, CH_2Cl_2 and THF, but only sparely soluble in MeCN and hexane.

The ^{1}H NMR spectra indicated that the methylene protons of the $C_6H_4(CH_2)_2$ unit in **2**, **3** and **6** are non-equivalent, exhibiting two doublets for **2**, **3** and four doublets for **6** in the range 3.8–4.2 ppm. The NMR spectra of **7** are not so informative because of the paramagnetism of this 17-electron ferracarborane. The ^{11}B NMR spectra of metallacarboranes with the C_2B_{10} system exhibited 2:2:1:1:2:2, 1:1:2:1:1:1:1:1:1 and 1:1:1:1:1:1:2:1:1 patterns for trivalent cobaltacarboranes **2**, **4** and **5** in the range −11 to +17 ppm, and a 1:1:1:1:1:1:1:1:1:1 pattern for divalent ferracarborane **6** in the range −22 to +24 ppm, respectively (Fig. 1). The deborated cobaltacarborane **3** showed a 1:1:2:2:2:1 pattern in the range −19 to −1ppm. It was noteworthy that as the ^{11}B NMR spectrum of **6** displayed ten resonances with the peak at 23.6 ppm assignable to the cage B bonded to THF, full assignment of the cage B atoms was thus achieved by careful analyses of the cross-peaks observed in the 2D ^{11}B–^{11}B spectrum.

Thermal rearrangement of the cage atoms is a very common phenomenon in d-block metallacarboranes of the C_2B_9 and C_2B_{10} systems [11,13]. As revealed by ^{11}B NMR spectra, **2** is stable even in refluxing dichlorobenzene (180 °C) for 3 days, indicating that CAd metallacarboranes are much more thermally stable than their CAp counterparts.



Scheme 2. Synthesis of cobalta- and ferra-carboranes with C_2B_9 system.

2.2. Structure

The solid-state structures of **2**–**7** were further confirmed by single-crystal X-ray analyses and are shown in Figs. 2–7. The $Cent_{Cp}$-M-$Cent_{CB}$ angles of **2**–**7** range from 171° to 176° (Table 1), suggesting a full-sandwich type of structures. This may be ascribed to the favorable interaction between metal d-orbitals and frontier orbitals of the carborane cage [14].

The solid-state structures of **2** show that there are two orientations for the $C_6H_4(CH_2)_2$ moiety, in which **2a** recrystallized from CH_2Cl_2 adopts the upward arrangement, and **2b** recrystallized from THF adopts the downward arrangement. These may result from the crystal packing forces in the crystal lattices. The metal atoms in **3** and **7** are more symmetrically bonded to the cage atoms than those in **2**, **4**–**6**. The average bond distances for M-C_{ring}, M-cage(C_2B_9) and M-cage(C_2B_{10}) fall in the range 2.04–2.09, 2.06–2.09 and 2.13–2.15 Å, respectively (Table 1). The relatively longer M-cage atom distances in the C_2B_{10} system is mainly due to the larger size of the C_2B_4 bonding face.

The average M-cage(C_2B_{10}) distances of 2.138(5) Å in **2a**, 2.150(3) Å in **2b**, 2.142(2) Å in **4**, 2.151(7) Å in **5** and 2.132(4) Å in **6** are close to the corresponding values of 2.147(3) Å in (η^5-C_5H_5)Co(η^6-$C_2B_{10}H_{12}$) [15], 2.152(3) Å in (η^5-C_5H_5)Co(η^6-$C_2B_{10}H_4Me_8$) [16] and 2.137(2) Å [(η^5-C_5H_5){η^6-[$(CH_2)_3$]$C_2B_{10}H_{10}$}]Co [9c]. The average M-cage(C_2B_9) distances of 2.055(7) Å in **3** and 2.092(5) Å in