Journal of Organometallic Chemistry 749 (2014) 188–196

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Hypoelectronic metallaboranes: Synthesis, structural characterization and electronic structures of metal-rich cobaltaboranes

Kiran Kumarvarma Chakrahari [a], Dudekula Sharmila [a], Subrat Kumar Barik [a], Bijan Mondal [a], Babu Varghese [b], Sundargopal Ghosh [a,*]

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
[b] Sophisticated Analytical Instruments Facility, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

*Article history:*
Received 1 August 2013
Received in revised form
21 September 2013
Accepted 23 September 2013

*Keywords:*
Metallaborane
Icosahedron
Hypoelectronic
Cobaltaborane

ABSTRACT

Reaction of $[Cp^*CoCl]_2$ ($Cp^* = \eta^5$-$C_5Me_5$) with $[LiBH_4 \cdot THF]$ in toluene at −70 °C, followed by thermolysis with 2-mercaptobenzothiazole ($C_7H_5NS_2$) in boiling toluene led to the isolation of a range of cobaltaborane clusters, $[(Cp^*Co)_2B_7H_6OMe]$, **1**; $[(Cp^*Co)_3B_8H_7R]$, **2a**, **b** (**2a**: R = H; **2b**: R = Me); $[(Cp^*Co)_3B_8H_8S]$, **3** and $[(Cp^*Co)_2B_4H_4RR']$, **4a–d** (**4a**: R, R′ = H; **4b**: R = Me, R′ = H; **4c**: R = H, R′ = Me and **4d**: R, R′ = Me). In parallel to the formation of compounds **1–4**, the reaction also yielded known $[(Cp^*Co)_3B_4H_4]$ in good yield. Compound **1** may be considered as 9-vertex hypoelectronic cluster with $C_1$ symmetry, where cobalt atoms occupy the degree 5 vertices. All the dicobaltaboranes **4a–d** contains two $\mu_3$-H protons and found to be very reactive. As a result, one of them (**4a**) when reacted with $Fe_2(CO)_9$ and sulfur powder yielded, almost immediately, $[(Cp^*Co)_2B_4H_5SFe_3(CO)_9]$, **5** and $[(Cp^*Co)_2B_3H_3(\mu$-$CO)Fe(CO)_3]$, **6**. All the new compounds have been characterized in solution by mass, $^1H$, $^{11}B$, $^{13}C$ NMR spectroscopy and elemental analysis. The structural types were unequivocally established by X-ray crystallographic analysis of compounds **1–6**. Density functional theory (DFT) calculations on the model compounds **1′** and **2′** (**1′**, and **2′** are the Cp analog of **1**, and **2a** respectively, Cp = $C_5H_5$) yield geometries in agreement with the structure determinations. The existence of large HOMO–LUMO gap of these molecules rationalizes the *isocloso* description for **2a**. Bonding patterns in the structure have been analyzed on the grounds of DFT calculations.

## 1. Introduction

The range of metallaborane compounds synthesized by us and others continues to grow as does the synthetic methods [1–5]. Several approaches to the expansion of cluster networks containing main group or transition metal fragments have received considerable attention [6–9]. For example, condensation involving monoborane reagents, insertion or fragmentation involving borane or metal carbonyl fragments and cluster fusion [10]. Unfortunately, in most of the methods, the great majority of metallaboranes, generated in low yield, have low metal to boron ratio [11–15]. Although the mechanistic details of the fusion process in cluster growth reaction are not yet understood, it has potential practicality as synthetic method [16–20]. Applying this methodology, we have synthesized a number of metallaboranes and derivatives [21–24].

A regular exercise both in metallaborane and metallacarborane chemistry is the formal substitution of heteroatom or metal fragments for BH or CH units, that often lead to cluster of higher stability than their parent molecules [25]. Among the hundreds of metallaboranes and their derivatives reported till date [26–29], there are good number of mono- or dimetallaheteroboranes with 12-vertices known and none with more metals [30–32]. The lack of larger metal rich metallaboranes and the recent findings in group 9 metallaboranes of Rh [33], led us to renewed interest toward the isolation of cobalt-rich metallaboranes with larger number of vertices. Although the objective of isolating higher vertex clusters was not achieved, novel *closo* and *isocloso*-metal rich cobaltaboranes have been isolated. We describe herein the synthetic findings together with crystallographic structure determination of several *closo*- and *isocloso*-cobaltaboranes.

## 2. Results and discussion

### 2.1. Synthesis and characterization of compounds 1–4

As shown in Scheme 1, the reaction of $[Cp^*CoCl]_2$ with excess of $[LiBH_4 \cdot THF]$ in toluene at −70 °C, followed by thermolysis in

---

[*] Corresponding author.
*E-mail address:* sghosh@iitm.ac.in (S. Ghosh).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.09.032

presence of 2-meracaptobenzothiazole in boiling toluene for 3 days yielded cobaltaboranes **1**–**4**. Although they are produced in a mixture, these compounds can be separated by TLC which allowed spectroscopic and structural characterization of pure materials. Note that compounds **1**, **2a**, **b** and **4a**, **b** can also be isolated if an *in-situ* generated intermediate, obtained from the reaction of $[Cp^*CoCl]_2$ with $[LiBH_4{\cdot}THF]$, thermolyzed in absence of 2-mercaptobenzothiazole. Thus, the 2-mercaptobenzothiazole acts as a source of sulfur that eventually yielded **3**. Compounds **1**–**4** are reasonably air stable and can be handled in air for extended periods without apparent change, especially in the pure crystalline state. Spectroscopic and structural characterizations of **1**–**4** from the NMR, IR, mass spectrometry and X-ray diffraction studies are discussed below.

### 2.1.1. *$[(Cp^*Co)_2B_7H_6(OMe)]$, **1***

Compound **1** has been isolated as orange solid in 5% yield. The $^{11}$B NMR spectrum exhibits seven chemical shifts at $\delta = 151$, 110, 103, 45, 31, 15 and 10 ppm, suggesting the absence of symmetry in the molecule. In addition to the signal attributable to the Cp* protons, the presence of methoxy protons were observed in the $^{1}$H NMR spectrum. The presence of Cp* and methoxy moieties were further confirmed by a $^{13}$C NMR spectrum. The IR spectrum of **1** feature medium absorption bands in the range of 2461–2490 cm$^{-1}$ due to the terminal B–H stretches. From the mass spectral analysis combined with IR, $^{11}$B, $^{1}$H, and $^{13}$C NMR spectra, **1** is formulated as $[(Cp^*Co)_2B_7H_6(OMe)]$.

The framework geometry of **1** (Fig. 1) became clear when a solid state X-ray structure was determined. Six among the seven boron atoms have terminal hydrogen atoms and one is attached to a methoxy group. The boron–oxygen bond length of 1.365(6) Å is significantly shorter compare to those observed in alkoxy-metallaborane clusters $[(Cp^*Mo)_2B_5(\mu_3\text{-}OEt)H_6(OBu)]$ (1.401(9) Å) and $[(Cp^*Mo)_2B_5H_8(O^iPr)]$ (1.400(7) Å) [34,35]. Although the average B–B (1.79 Å) and Co–B bond lengths (2.05 Å) are analogs to those observed in cobaltaborane clusters [36–38], the Co1–B6 bond length of 2.230(5) Å and B3–B5 bond length of 2.078(8) Å are significantly longer. This anomaly of bond distances led us to perform computational study to probe the electronic structure of compound **1**. The DFT molecular study of **1′** (**1′**: Cp analog of **1**; Fig. S1, Supplementary information) shows a strong bonding interaction between Co1 and B3 and a weak bonding interaction between B3 and B5 (HOMO) (Fig. 2). Furthermore, the bonding interaction along the Co2–B1 bond and anti-bonding interaction along the B2–B7 bond (HOMO, HOMO − 1) shows the possibility of a DSD (Diamond–Square–Diamond) rearrangement from its *closo* structure. The ionization potential energy and NICS values further support the stability of hypoelectronic **1′** (Table S1, Supplementary information). Further the DFT calculations at BP86/6-31g* level reproduces the experimental geometry **1′**. The computed $^{11}$B chemical shift values of **1′** using gauge-including atomic orbital density functional theory [GIAO–DFT] method at the B3LYP/6-31g* level show satisfactory match with the experimental values (Table S2).

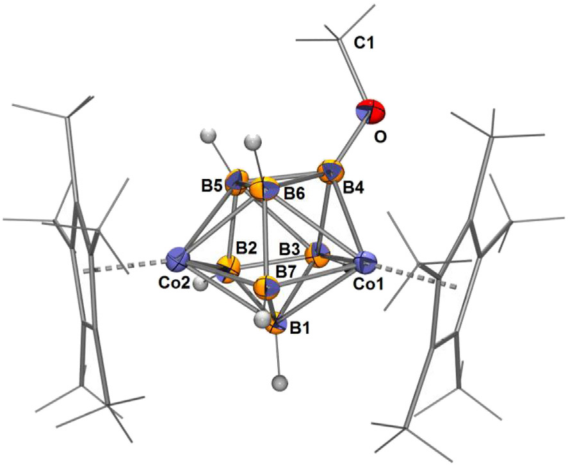
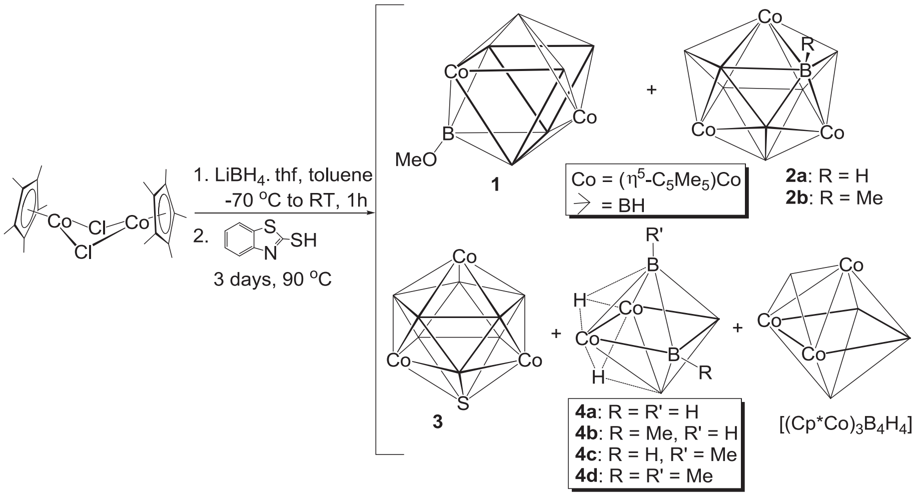


**Fig. 1.** Molecular structure and labeling diagram for **1**. Selected bond lengths (Å) and angles (°): Co(1)–B(7) 1.952(5), Co(1)–B(4) 1.959(5), Co(1)–B(1) 2.123(5), B(6)–Co(1) 2.230(5), Co(2)–B(7) 1.946(5), B(3)–B(5) 2.078(8), B(4)–O(1) 1.365(6), B(7)–Co(1)–B(6) 49.74(19), B(3)–Co(1)–B(6) 78.5(2).

The molecular structure of **1** does not display the structural motif expected for a classical nine-vertex *closo*-polyhedra. As shown in Chart 1, the rational shape was resultant from the *closo* metal-free borane deltahedra by one DSD, generating degree 5 vertex for the two Co atoms. Four of the B atoms occupies the five connected vertex, whereas rest of the B atoms are having vertex connectivity of four. The driving force behind this kind of rearrangement may be due to the preference of transition metals for higher-degree vertices than main group atoms [39]. Consequently,



**Scheme 1.** Synthesis of metal-rich cobaltaboranes, and cobaltathiaborane.