Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 251 (2007) 2452–2476
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Advances in the chemistry of carboranes and metallacarboranes with more than 12 vertices

Liang Deng, Zuowei Xie *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Received 12 October 2006; accepted 11 February 2007
Available online 15 February 2007

Contents

Abstract

Boron clusters with more than 12 vertices showing a very rich and diverse chemistry were confined to the 13- and 14-vertex metallacarboranes until 2003. Very recently, significant progress in the syntheses of 13- and 14-vertex carboranes has been made, leading to the preparation of 15-vertex metallacarboranes. These studies open up new possibilities for the development of polyhedral clusters of extraordinary size. This review summarizes the advances in this growing research field since the successful preparation of the first 13-vertex metallacarborane. Achievements, problems and perspectives are discussed in this article.

Keywords: Carborane; Metallacarborane; Lanthanide; *p*-Block metal; Supercarborane; Transition metal

1. Introduction

The chemistry of carboranes and metallacarboranes has received considerable attention since their emergence in the 1960s [1,2]. Efforts of almost half a century in this area have resulted in the extensive studies on the synthesis, structure, reactivity, and application of these clusters [3–21]. Progress in this field has been discussed in a number of reviews [8–21] and monographs [3–7]. This review will focus specifically on the advances in the chemistry of carboranes and metallacarboranes with more than 12 vertices. When the cluster size is concerned, icosahedral and sub-icosahedral carboranes dominate the research activities in the past five decades [3–21], and carboranes with more than 12 vertices (so called supercarbo-

* Corresponding author. Tel.: +852 26096269; fax: +852 26035057.
E-mail address: zxie@cuhk.edu.hk (Z. Xie).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.02.009

ranes) were not known before 2003 [22]. It is only in recent years that significant progress been made in the chemistry of supercarboranes [23,24]. Subsequently, 15-vertex metallacarboranes were also prepared in 2006 [25,26]. These new achievements will be included in this review.

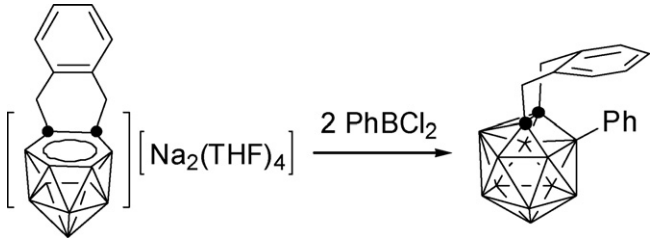
If no atom is indicated in the polyhedral structures shown in the following schemes, the vertex is a BH group. The black dot in the drawings represents a carbon atom. If a vertex contains an atom other than B and C, the heteroatom is shown explicitly. There are two cage-carbon-atom arrangements in carboranes, the carbon-atoms-adjacent (CAd) isomers where the cage carbon atoms occupy adjacent positions, and the carbon-atoms-apart (CAp) isomers where the cage carbon atoms are separated by at least one boron atom. For easy reference, all structurally characterized carboranes and metallacarboranes with more than 12 vertices are compiled in Tables 1–3 and included in the Supporting Information.

2. Carboranes with more than 12 vertices

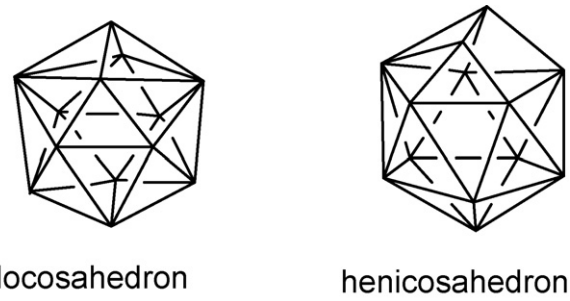
2.1. Thirteen-vertex carboranes

Although *closo*-carboranes of the general formula $C_2B_nH_{n+2}$ have been known for $n = 3$–10 since the 1960s [3,4], knowledge of *closo*-carboranes and -boranes with more than 12 vertices has been limited merely to their possible cage geometries predicted by theoretical studies [27]. Recent calculations on boranes $B_nH_n^{2-}$ show that the overall stability of these clusters increases as n gets larger with the exception of $n = 12$ which is much more stable than the others [28]. Such an "icosahedral barrier" is often used to account for the failure in the syntheses of supercarboranes [22,29,30].

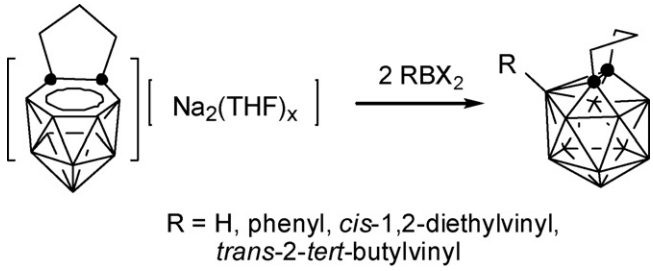
Recognition of the relatively lower reducing power of CAd carborane anions over the CAp counterparts offers a very valuable entry point to the synthesis of supercarboranes [31]. Accordingly, the first 13-vertex carborane 1,2-$C_6H_4(CH_2)_2$-5-Ph-1,2-$C_2B_{11}H_{10}$ was prepared by the Welch group in 6% yield from the reaction of [7,8-$C_6H_4(CH_2)_2$-7,8-$C_2B_{10}H_{10}$]Na_2 with $PhBCl_2$ [22] (Scheme 1). Single-crystal X-ray analyses show that the carborane cage of this molecule adopts a henicosahedral geometry, which is different from the predicted docosahedral geometry of $B_{13}H_{13}^{2-}$ [28]. DFT calculations reveal that the henicosahedral structure is preferred over the docosahedron by 7.4 KJ mol^{-1} for the 13-vertex carborane 1,2-$C_2B_{11}H_{13}$ (Scheme 2).



Scheme 1.



Scheme 2.



Scheme 3.

Subsequently, the Xie group synthesized a series of 13-vertex carboranes by treatment of the CAd carborane dianionic salts with borane dihalides in 7–32% yields using a trimethylene bridged carborane as the starting material [23,24] (Scheme 3). Non-donor solvents and less bulky borane reagents often offer higher synthetic yields. Fig. 1 shows the molecular structure of 1,2-$(CH_2)_3$-3-Ph-1,2-$C_2B_{11}H_{10}$ which is similar to that of 1,2-$C_6H_4(CH_2)_2$-5-Ph-1,2-$C_2B_{11}H_{10}$ [22]. The only difference in

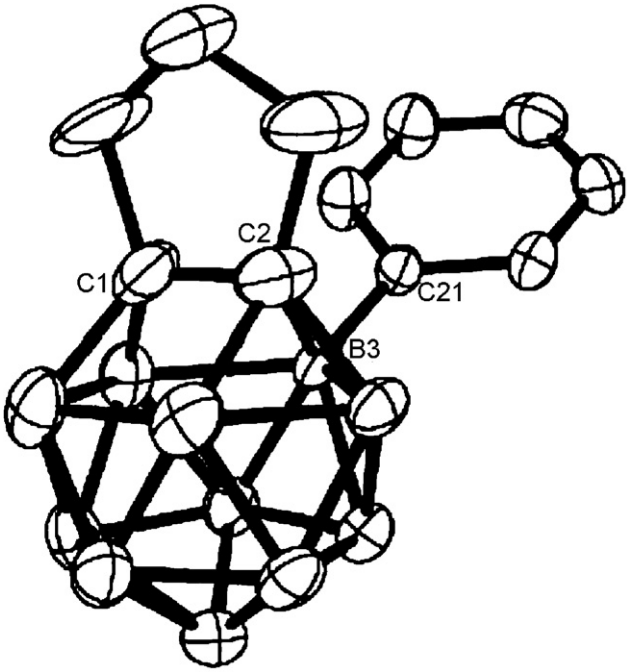


Fig. 1. Structure of 1,2-$(CH_2)_3$-3-Ph-1,2-$C_2B_{11}H_{10}$ reproduced by permission of The American Chemical Society from Ref. [24].