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Nano and dendritic structured carboranes and metallacarboranes: From materials to cancer therapy

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ABSTRACT

An account of the current research carried out in our laboratories is presented. Included is the incorporation of several group 14 elements into charge-compensated carboranes. These species present a bonding pattern not found in other main group carboranes. In addition to our continuing studies of the syntheses and structures of organometallic compounds, the use of these compounds as catalysts and catalyst precursors has been investigated. The isotopic exchange reactions between ^{10}B enriched boron hydrides with naturally abundant boranes catalyzed by Ru(0) nanoparticles has been studied. The Ru(0) nanoparticles were obtained by the reduction of $[CpRuCp^*RuCp^*]PF_6$ ($Cp^* = C_5Me_5$) with hydrogen and stabilized by the ionic liquid trihexyltetradecylphosphonium dodecylbenzenesulfonate [THTdP][DBS]. This was found to be an excellent, long lived catalyst for the exchange reaction of B-10 enriched diborane and naturally abundant decaborane(14). Other approaches to the production and use of nano-metal catalysts have also been explored. The reduction of the iridium carborane, $(PPh_3)_2IrH(7,8\text{-}C_2B_9H_{11})$ with hydrogen in the presence of trihexyltetradecylphosphonium methylsulfonate, [THTdP][MS], produced an Ir(0) nanoparticles that catalyzed the phenylborolation as did our Ir(sal = N-R = salicylaldiminato; COD = cyclooctadiene complex. Progress in the use of single wall carbon nanotubes (SWCNT) as boron delivery agents was also discussed.

1. Introduction

Our research has dealt with two important aspects of inorganic chemistry: our continued interest in the structure and properties of the heterocarboranes, and, more recently in the use of metallacarboranes as precursors in the syntheses of nano-metal catalysts. This Account summarizes some of our more important results.

One class of organometallic compounds that closely parallels the metallocenes are those in which the cyclopentadienide anion, $[C_5R_5]^-$, is replaced by a heteroborane. Boranes are mixed hydrides of boron and hydrogen where the boron atoms are contained in electron deficient clusters. These clusters usually are associated with high negative charges. For example the general formula for an *n* vertex closed structure (*closo*) is $[B_nH_n]^{2-}$, the more open borane structures have increasingly higher negative charges. As a result, these compounds are difficult to work with. However, if a three electron $[B–H]^-$ vertex is replaced by a neutral three electron vertex, such as a [C–R] group, there is no change in structure, but the charge is decreased by one. Some of the most encountered heteroboranes are the dicarbaboranes (dicarborane) in which the cluster charge is decreased by two; the general formula for an $n+2$ vertex *closo*-dicarborane is $C_2B_nH_{n+2}$. If the primary bonding atom of the group replacing a [H–B] vertex is a metal, the cluster is referred to as a metallaborane, or more likely to be encountered, a metallacarborane. There are a simple, elegant set of rules, culminating in the Polyhedral Skeletal Electron Pair counting rules, for predicting the structures of the heteroboranes from the composition of the clusters [1–5]. Most of the metallacarboranes in this account are those with the general formula, $MC_2B_nH_{n+2}$ ($n = 4, 9$) [5d], having pentagonal bipyramidal and icosahedral structures, respectively. These can be viewed as coordination complexes between the metal, M^{2+}, and a $[nido\text{-}C_2B_nH_{n+2}]^{2-}$ ligand, in which the metal group is bonded to the open C_2B_3 pentagonal face of the carborane, in much the same way as the cyclopentadienide, $[C_5R_5]^-$, bonds to metals in the metallocenes. Indeed, the primary metal-bonding carborane orbitals are a set of three, filled, π-type orbitals delocalized about the pentagonal face of the carborane that are very similar to those of $[C_5R_5]^-$; this was initially recognized by Hawthorne in the syntheses of the first metallacarboranes [6]. There are two

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different arrangements of the atoms on the C_2B_3 face, one in which the carbons are next to one another (carbons adjacent) and another in which they are separated by a boron atom (carbons apart). They both seem to bond equally well with metals, but the latter is thermodynamically more stable [4,5]. Analogous to that found for the metallocenes, metallacarboranes have been reported in which the metal group bonds to a single carborane cage, to give half-sandwich compounds, or that occupy vertices of two carboranes, to give full-sandwich (*commo*-) compounds. We have been exploring these compounds as potential catalysts, or catalyst precursors, as well as exploring their use as boron delivery agents in BNCT.

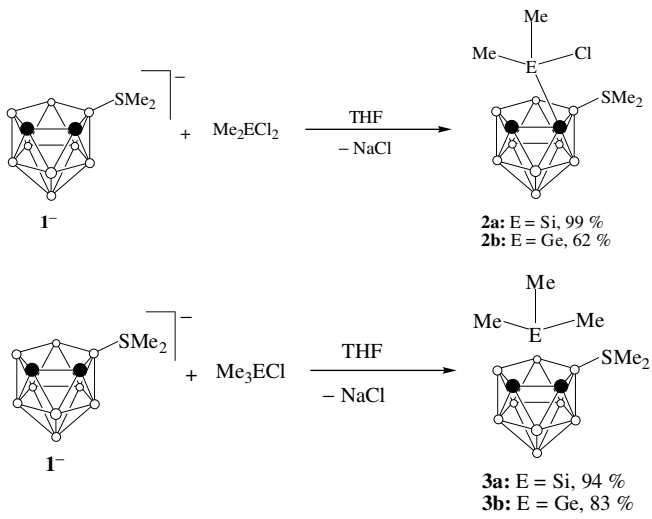
One of the most startling developments in the last few decades, is in the syntheses and catalytic applications of nano-scaled particles prepared from groups 8–10 elements [7]. We have studied the use of these nanoparticle catalysts, derived from the corresponding metallacarborane precursors.

Our results led us to conclude that there remains a wealth of unexplored research that still to be done on the application of metallacarboranes to problems in catalysis and medicine. The most significant results of this research are presented in this account.

2. Chemistry of main group metallacarboranes

Main group metallacarboranes in which a silicon or germanium occupies an apical position above a [*nido*-$(RC)_2B_nH_n]^{2-}$ cage are among the earliest reported [5a,b]. These compounds can exist as either half-sandwich or distorted full-sandwich species with the group 14 element, in both +2 and +4 oxidation states, respectively. In the corresponding metallocenes, only the +2 is found. The dinegative charge on the carborane ligands might play a key role in determining the oxidation state of the metal or it may be that the heteronuclear nature of the bonding face is important. Therefore, it is an open question as to what oxidation state would be favored when the group 14 element would bond to a monoanionic carborane ligand, such as a charge-compensated carborane. This curiosity led us to react the charge-compensated ligand, [9-SMe_2-7,8-$C_2B_9H_{10}]^{1-}$ (**1**$^-$) with Me_2ECl_2 and Me_3ECl (E = Si, Ge) [8]. Scheme 1 shows that a 1:1 stoichiometric reaction takes place to form η^1-8-EMe_2Cl-9-SMe_2-7,8-$C_2B_9H_{10}$ (E = Si(**2a**), Ge(**2b**)) and (EMe_3)-9-SMe_2-7,8-$C_2B_9H_{10}$, (E = Si(**3a**), Ge(**3b**)) even in the presence of excess carborane [8].

Compounds **2a** and **2b** were found to be isostructural (Figs. 1 and 2) with the $EClMe_2$ group bonded to the cage carbon that is adjacent to the Me_2S–B vertex [8]. A comparison of the structures of **2a** and **2b** with the precursor [9-SMe_2-7,8-$C_2B_9H_{10}]^-$ showed that coordination by the $EClMe_2$ causes a lengthening of the cage carbon bonds from 1.535 Å to 1.818 Å and 1.844 Å, respectively; the C(7)–B(9) bonds are also elongated, from 1.598 Å to 1.792 Å and 1.794 Å (see Fig. 1).



Scheme 1. Syntheses of group 14 metallacarboranes.

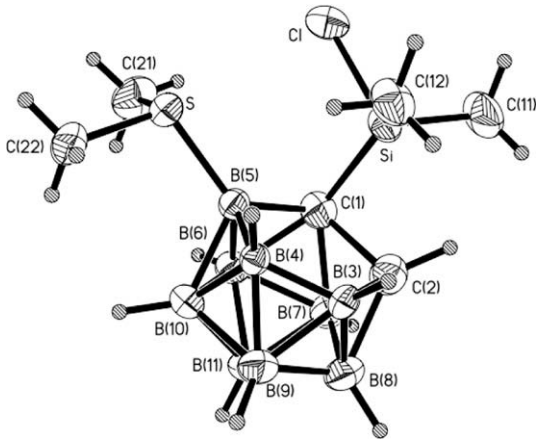


Fig. 1. Crystal structures of group 14 (Si) metallacarboranes.

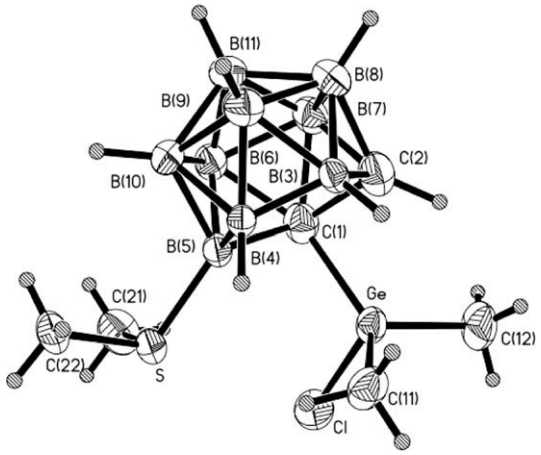


Fig. 2. Crystal structures of group 14 (Ge) metallacarboranes.

The bonding of the $EClMe_2$ groups to the cage carbon is interesting and atypical in that the carbon atom already has a terminal hydrogen. It is an open question as to whether the 0.3 Å elongation of the C_{cage}–C_{cage} bond constitutes a bond rupture.

It was found that the complex, ($SiMe_3$)(9-SMe_2-7,8-$C_2B_9H_{10}$), was highly reactive towards other metal halides and is potentially useful as a carborane transfer agent as evidenced by the formation of the corresponding charge-compensated Fe(II)-sandwich complex (Scheme 2). It is of interest that the Fe(II) is sandwiched between two η^5-bonding carboranes, as seen in Fig. 3 [8].

3. Nanoparticles-catalyzed isotopic exchange reactions

Nanoscale metal particles have been attracting much attention and are widely explored for their intriguing chemical and physical properties, as well as potential applications [9]. The extremely high surface areas and the subsequent high density of active sites of these nanoparticles make them more attractive catalysts than the bulk metals [10,11]. Transition metals such as Ru, Os, Ir, and Rh, were found to activate B–H bonds in boron clusters to form metal–boron (M–B) bonds [12]. Also, carboranes and boron hydrides