Group 9 metallatelluraboranes: Comparison with their sulfur analogues

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ABSTRACT

The lowest energy structures for the Group 9 metallachalcaboranes $CpMEB_{n-2}H_{n-2}$ (M = Co, Rh, Ir; E = S, Te) are found by density functional theory to have a central *closo* MEB_{n-2} deltahedron consistent with their $2n + 2$ skeletal electrons. Structures having metal atoms at degree 5 vertices and sulfur atoms at degree 4 vertices are clearly energetically preferred. However, for the 9- and 10-vertex metallatelluraboranes $CpMTeB_{n-2}H_{n-2}$ ($n = 9, 10$; M = Co, Rh, Ir) otherwise related structures having tellurium atoms at degree 4 and degree 5 vertices are energetically comparable. The low-energy 11-vertex $CpMEB_9H_9$ structures are all based on the 11-vertex *closo* deltahedron with a unique degree 6 vertex. However, in many of the low-energy 11-vertex structures one of the edges connecting the degree 6 vertex with an adjacent degree 5 vertex is stretched to a non-bonding distance leading to an *isonido* structure having a quadrilateral face. The three lowest energy structures for the 12-vertex $CpMEB_{10}H_{10}$ (M = Co, Rh, Ir; E = S, Te) systems are the three possible icosahedral structures with the energy ordering *ortho < meta < para*.

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1. Introduction

The fundamental building blocks of polyhedral borane chemistry are the most spherical *closo* deltahedra that have vertices as similar as possible (Fig. 1) [1,2]. Such deltahedra include the 6-vertex octahedron and the 12-vertex icosahedron as the two regular *closo* deltahedra. The Wade-Mingos rules [3–6] imply that an *n*-vertex *closo* deltahedron has $2n + 2$ skeletal electrons where a BH vertex is a donor of two skeletal electrons. Thus the borane dianions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) as well as isoelectronic neutral species, such as the dicarbaboranes $C_2B_{n-2}H_n$ in which each CH vertex contributes three skeletal electrons, exhibit *closo* deltahedral structures. Furthermore, a bare chalcogen atom (sulfur, selenium, and tellurium) with a single external lone pair is a donor of four skeletal electrons. Thus neutral $EB_{n-1}H_{n-1}$ (E = S, Se, Te) species also have $2n + 2$ skeletal electrons and generally exhibit *closo* deltahedral structures.

Deltahedral metallaborane derivatives in which one or two vertices are replaced by transition metal moieties were first synthesized by Hawthorne and co-workers using decaborane, $B_{10}H_{14}$, as the boron source [7]. Shortly thereafter, smaller deltahedral metallaboranes were synthesized by Grimes and coworkers using B_5H_9 as the boron source [8]. In this connection a cyclopentadienylcobalt (CpCo) vertex is a donor of two skeletal electrons like a BH vertex. Replacing one or two BH vertices in the dicarbaborane derivatives with CpCo vertices gives the cobaltadicarbaboranes $CpCoC_2B_{n-3}H_{n-1}$ and $Cp_2Co_2C_2B_{n-4}H_{n-2}$ as stable species exhibiting *closo* deltahedral structures. In addition, the experimentally known icosahedral cobaltathiaboranes, $CpCoSB_{n-2}H_{n-2}$ ($n = 10, 12$) are derived from the metal-free thiaboranes $SB_{n-1}H_{n-1}$ by replacement of a BH group by a CpCo moiety [9,10].

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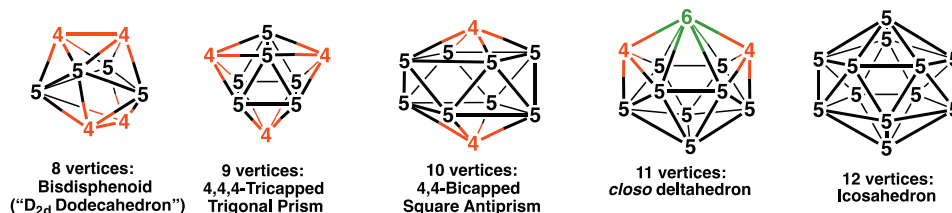*E-mail addresses:* alupan@chem.ubbcluj.ro (A. Lupan), rbking@chem.uga.edu (R.B. King).

Fig. 1. The most spherical *closo* deltahedra having 8 to 12 vertices indicating the degree of each vertex. The vertices are also color coded with degree 4, 5, and 6 vertices as red, black, and green, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Polyhedral metallachalcaboranes of the type $CpMEB_{n-2}H_{n-2}$ (M = Co, Rh, Ir; E = S, Se, Te) of the group 9 metals represent species having the $2n + 2$ skeletal electrons expected by the Wade-Mingos rules [3–6] to exhibit *closo* deltahedral structures. In such series both the effects of changing the group 9 transition metal and of changing the chalcogen can be examined. In view of the significant differences between the inorganic chemistry of sulfur and tellurium, particularly regarding their hypervalent chalcogen(IV) derivatives, comparison of otherwise similar metallathiaboranes and metallatelluraboranes is of interest. In our previous work on cobaltadipnictaboranes of the type $CpCoE_2B_{n-3}H_{n-3}$ (E = P [11], Bi [12]) we have found significant differences between the phosphorus and bismuth derivatives. Thus the lowest energy cobaltadiphosphaboranes $CpCoP_2B_{n-3}H_{n-3}$ are found to have their phosphorus atoms as far apart as possible. However, the lowest energy cobaltadibismaboranes $CpCoBi_2B_{n-3}H_{n-3}$ have structures forming a BiBi edge of the polyhedron.

Experimentally known high nuclearity metallatelluraboranes are of two types (Fig. 2). Icosahedral species of the type $[M]TeB_{10}H_{10}$ ($[M] = (Et_3P)_2Pt$ [13], $(Me_2PhP)_2Pd$ [14], $Cp*Rh$ [15], $(\eta^6\text{-}Me_6C_6)Ru$ [15] $(\eta^7\text{-}C_7H_7)Mo$ [16], Ph_3PAu [17]), can be synthesized by reactions of the *nido*-telluraundecaborate anion $[TeB_{10}H_{11}]^-$ with suitable transition metal derivatives. The dimetalladitelluraboranes $Cp*_2M_2Te_2B_{n-4}H_{n-4}$ ($Cp* = \eta^5\text{-}Me_5C_5$; M = Mo, $n = 4$; M = W, $n = 5$) are obtained by treatment of $Cp*MCl_4$ with $LiBH_4$ followed by heating with tellurium [18,19]. The $Cp*_2M_2Te_2B_{n-4}H_{n-4}$ structures are oblate deltahedral structures with at least one or two degree 3 tellurium vertices. These structures are thus similar but not identical to the *oblatocloso* dirhenaborane $Cp*_2Re_2B_{n-2}H_{n-2}$ structures [20–23] which have no degree 3 vertices.

We now report theoretical studies on the $CpMEB_{n-2}H_{n-2}$ ($8 \leq n \leq 12$; M = Co, Rh, Ir; E = S, Te) systems. In accord with their $2n + 2$ skeletal electrons, the most spherical *closo* deltahedral structures (Fig. 1) are almost always energetically preferred. However, isomeric structures with different arrangements of the heteroatoms on the central MEB_{n-2} *closo* deltahedral framework can have very different relative energies. In addition, the 11-vertex *closo* $CpMEB_9H_9$ structures, which necessarily have a degree 6 vertex, can have "fragile" edges leading from the unique degree 6 vertices. Such fragile edges can stretch beyond bonding distance thereby converting the *closo* 11-vertex structure to an *isonido* structure with a
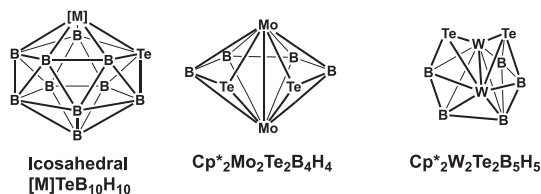
quadrilateral face and no vertices of degree higher than 5. Such a fragile Fe–B edge from the degree 6 iron vertex stretching to a nonbonding 2.636 Å was found experimentally in the 11-vertex *closo* $CpFeP(CH_3)CHB_8H_8$ structure, synthesized and structurally characterized by Sneddon and co-workers [24], and later studied theoretically by our group [25] (Fig. 3).

2. Theoretical methods

The initial chemical structures investigated in this study are derived from the borane dianions $B_nH_n^{2-}$ by systematically substituting a BH vertex with a CpM unit (M = Co, Rh, Ir) followed by the replacement of an additional boron atom with S/Te atoms in various polyhedral frameworks. This leads to 2394 initial starting structures of the type $CpMEB_nH_n$ (M = Co, Rh, Ir; E = S, Te; $n = 8$ to 12) (see the Supporting Information).

Geometry optimizations of these initial structures were carried out using the B3LYP DFT functional coupled with the SDD (Stuttgart Dresden ECP plus DZ) basis set for iridium, rhodium, and tellurium and the double zeta 6-31G(d) basis set for the lighter atoms as implemented in the Gaussian09 suite of programs [26]. All optimized structures were characterized by harmonic vibrational frequencies. Saddle point structures with imaginary vibrational frequencies were reoptimized by following the normal modes in order to obtain genuine minima. The energetically most stable isomers were further optimized by employing the PBE0 DFT functional and the def2-TZVP//SDD basis sets. In order to refine further the energies, coupled cluster single point energy calculations were performed on the lowest energy isomers using the DLPNO-CCSD(T) coupled cluster method [27–40] and the def2-QZVP//SDD basis sets as implemented in the ORCA 3.03 software package [33,41–48]. The final energies were then corrected for zero-point energies obtained from the PBE0/(def2-TZVP//SDD) calculations. All of the resulting structures are singlets having substantial HOMO-LUMO gaps ranging from 3.6 to 5.9 eV. (see the Supporting Information) with the highest values corresponding to the lowest energy structures.

The shorthand notation $B(n-2)ME\text{-}x$ was assigned to all structures discussed in this work where **n** is the total number of polyhedral vertices, and **x** is the energy ranking of the structure on the potential energy surface of the $CpCoSB_{n-2}H_{n-2}$ system. Only the lowest energy and thus potentially chemically significant structures are discussed in detail. More comprehensive lists of structures,
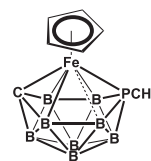

Fig. 2. Structures of the known metallatelluraboranes ($[M] = (Et_3P)_2Pt$, $(Me_2PhP)_2Pd$, $Cp*Rh$, $(\eta^6\text{-}Me_6C_6)Ru$, $(\eta^7\text{-}C_7H_7)Mo$, Ph_3PAu). External groups (H on B and Cp* on Mo and W) are omitted for clarity.

Fig. 3. The experimentally known 11-vertex $CpFe(PCH_3)CHB_8H_8$ structure with the fragile Fe–B edge indicated by a dashed line. External hydrogen atoms are omitted for clarity.