

Summary

Habilitation Thesis

Unusual metallaborane and metallocarborane clusters and their skeletal bonding

This habilitation thesis reviews some of the scientific results obtained by the author, Alexandru Lupan, after obtaining the Ph.D. The scientific activity of the author is in the area of molecular modeling with a focus on the investigation of cluster compounds. The most important class of such molecules that have been investigated are the metallaboranes and related clusters. They exhibit unusual polyhedral structures that challenge concepts of chemical bonding. Interactions involving metal atoms in a cluster can be the basis of novel optical, magnetic, and electronic properties. The general objective of this research is the fundamental understanding of the structure, bonding, thermochemistry, and chemical reactivity of polyhedral clusters, particularly metallaboranes, metallocarboranes as well as other types of main group and transition metal clusters. Computational approaches based on quantum chemistry and particularly density functional theory allow us to explore such areas of chemistry beyond those that are currently accessible experimentally. In order to understand the underlying basis for such structures in the last 15 years the author and his team have performed comprehensive density functional studies. This thesis reviews the highlights of the work in the area of metallaborane and metallocarborane clusters.

Part I. Contributions to understanding the structure and bonding in metallaborane and metallocarborane polyhedral structures, summarizes some of the most important results obtained by the author, and is based on scientific articles published as first and/or corresponding author in some of the most prestigious journals of the field.

The first chapter of this part reviews in a concise manner the structural motifs that are specific to the polyhedral molecules namely the *closo*, *nido* and *arachno* structures as well as other related arrangements such as the *isocloso* or the *oblatocloso* structures and the

mechanism by which such clusters can interconvert. The second chapter presents the topological models for the skeletal bonding in such polyhedra which are necessary in order to understand the bonding in metallaborane structures. The computational results are presented from the chapter three onwards, starting first with the most classical clusters, namely the *closo* structures having $2n + 2$ skeletal electrons as is the case of the dinickelaboranes as well as dimetalladicarbaboranes of cobalt, rhodium and iridium. Replacing some of the boron and/or carbon vertices in the deltahedra by transition metal moieties can lead to deviations from sphericity in the energetically preferred structures since transition metal moieties, particularly those of the second and third row transition metals, energetically prefer higher degree vertices than boron and carbon atoms. Chapter four approaches such less spherical clusters – with the least deviation been the the *isocloso* arrangement. *Isocloso* clusters have $2n$ Wadean skeletal electrons with the simplest example being the the diferradicarbaboranes. *Isocloso* deltahedral metallaboranes have $2n$ rather than $2n + 2$ Wadean skeletal electrons suggesting skeletal bonding topology with only surface bonding using all $2n$ skeletal electrons. Density functional theory studies show that 10-vertex systems, in particular, favor the C_{3v} *isocloso* structure in systems with 20 Wadean skeletal electrons in contrast to an isomeric D_{4d} *closo* bicapped square antiprism structure. The final topic of this chapter is represented by the *isocloso* supraicosahedral metallaboranes having 14 and 16 vertices.

Chapter five moves the reader's attention even further into the area of hypoelectronicity, focusing on the *oblatocloso* dimetallaboranes, starting with the example of hypoelectronic dirhenaboranes. Such dirhenaboranes exhibit more extreme deviations from sphericity as compared with any of the previous examples. Thus their flattened oblate ellipsoidal deltahedral structures have degree 6 and even 7 rhenium vertices at sites of low deltahedral surface curvature and degree 4 and 5 boron vertices at sites of relatively high deltahedral surface curvature. The hypoelectronicity is then increased up to systems having $2n - 6$ skeletal electrons, as is the case of the dimolybda- and ditungstaboranes. The observation of the unusual high energy deltahedral dirhenaborane structures containing polyhedral surface rhenium-rhenium multiple bonds led us to investigate polyhedral surface metal-metal multiple bonds by designing structures containing pentalene ligands. The research was then expanded further, beyond dimetallaboranes, by investigating trimetalla- and tetrametallaborane structures. Comparing the 11-vertex deltahedra for the experimentally known tritungstaborane $Cp_3W_3B_8H_8$ and tetramolybdaborane $Cp_4Mo_4B_7H_7$ shows how the preference of the metals for higher vertex degrees (6 and 7) leaving the boron atoms at

vertices of lower 4 and 5 degrees can lead to considerable deviations from sphericity with relatively low curvature at the metal vertices and relatively high curvature at the boron vertices. This can suggest different paradigms for construction of such deltahedra. And finally, chapter six focuses on the hydrogen-rich dimetallaboranes. Such structures are based on *nido* polyhedra, which are obtained by removing a vertex from a *closo* deltahedron. The chapter then summarizes our extensive investigation of such hydrogen-rich dimetallaborane systems, having four extra hydrogen atoms and involving various transition metals.

Part II. Future projects and research directions is organized into two chapters. The first chapter summarizes the scientific contributions of the author starting with the scientific results that he obtained as undergraduate and graduate student, as part of the molecular modeling laboratory team of the Faculty of Chemistry and Chemical Engineering of the Babeş-Bolyai University, briefly reviewing the most important scientific results of his Ph.D. thesis. The presentation continues with some of the achievements of his postdoc period and then other areas of research interest are also presented, namely topics not related to the cluster molecules that are the topic of interest for the first part of this thesis. The next section of the respective chapter also presents briefly dr. Lupan's collaborations with other researchers - either from the Faculty of Chemistry and Chemical Engineering of the UBB or from other universities and especially collaborations with experimentalist colleagues in which his molecular modelling expertise has contributed to the research topics of his peers. And finally, the second chapter of the second part presents briefly some of the future topics of research which will contribute significantly to the development of this field.