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Structural, electronic and magnetic properties of some early vs late transition dimetallaborane clusters – A theoretical investigation

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Dedicated to Prof. Michael Mingos on the occasion of his 70th birthday in recognition of his major contributions to cluster chemistry.

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ABSTRACT

The strength of DFT methods in analyzing the electronic and magnetic properties of a series of dimetallaboranes of varied stoichiometry and architectural core, namely M_2B_3 , M_2B_4 and M_2B_5 with both early- and late-transition metals is demonstrated. In particular, the observed 1H and ^{11}B chemical shifts of most of the studied compounds are reproduced with a good accuracy of a few ppm at the DFT-GIAO BP86/TZ2P/SC level for the compounds with first-row transition metal elements and at the B3LYP/TZ2P/SO level for those with second- and third-row transition metal elements. This allows structural applications in elucidating the number and the location of bridging hydrogen atoms in experimentally poorly characterized metallaboranes such as $(Cp^*Cr)_2B_4H_8$.

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1. Introduction

Although the proven methods for the formation of compounds containing metal-boron bonds are rather limited, there are today a plethora of metallaborane compounds, which have been synthesized and characterized with nearly all the transition metals, early and late metals [1]. Among them, dimetallaboranes constitute a larger part, with almost one hundred of them known and structurally and/or spectroscopically characterized [2–23]. Although the chemistry of these dimetallaboranes is experimentally growing rapidly, theoretical studies on these species are still rather scarce, despite the need to investigate and rationalize viz., (i) their structural diversity, (ii) their thermal and kinetic stability, (iii) their isomeric preferences, (iv) their chemical bonding, (v) their spectroscopic properties, etc. In particular, quantum chemical computations of ^{11}B and 1H NMR chemical shifts have become one of the

principal means of characterization of metallaborane compounds. These computations can even sometimes “rival that of X-ray crystallography” [24]. Density-functional theory (DFT) computations for instance can nowadays provide usefully precise chemical shifts as a function of the geometrical structure [25]. This has been shown by the past for some metallacarboranes for instance [26–28]. Recently, we have used such methods to tackle with some success the structural, electronic, and NMR properties of specific examples of dimetallaboranes [29–32].

For the latter, accuracies of about 2–3 ppm were achieved for the computed ^{11}B chemical shifts at the B3LYP/TZ2P all-electron relativistic scalar ZORA level of theory. Indeed, we have shown that although they are very computationally demanding, ^{11}B NMR chemical shift calculations at this level of theory using BP86/TZ2P/SC optimized geometries improves considerably (by ca. 5–10 ppm) the computed values with respect to those obtained at the GGA/TZ2P all-electron relativistic scalar ZORA level, for early 4d and 5d transition metal-borane systems (dimolybdaboranes, ditantalaboranes) [29,30]. On the other hand, only 1–2 ppm of improvement is observed for the metallaboranes with late 4d transition metal (diruthenaboranes for instance) [31]. This drove us to look at the

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suitability of DFT methods using different GGA vs. hybrid functionals to accurately compute ^{11}B NMR chemical shifts in metallaboranes in general. For this purpose a series of dimetallaboranes of varied stoichiometry and architectural cores, namely M_2B_3 , M_2B_4 and M_2B_5 , with early and late transition metals has been chosen and studied (Chart 1). It would have been desirable to compare results on early- and late-transition-metal boranes with the same architecture, but it has been shown experimentally that early transition metals often lead to the formation of rather highly

condensed metallaborane clusters (of M_2B_4 and M_2B_5 core), such as compounds **1–14** (Chart 1) discussed in this work, for example [13,33,34] whereas late-transition elements usually form stable metallaboranes with more open structures (with M_2B_3 core), such as compounds **15–17** (Chart 1) discussed in this work, for example [35]. Here we report that the observed ^{11}B NMR chemical shifts are reproduced with a reasonable accuracy at the BP86/TZ2P/SC level for the $3d$ metallaboranes. On the other hand, the B3LYP/TZ2P/SO level (SO = spin-orbit) is necessary for $4d$ and $5d$ metallaboranes

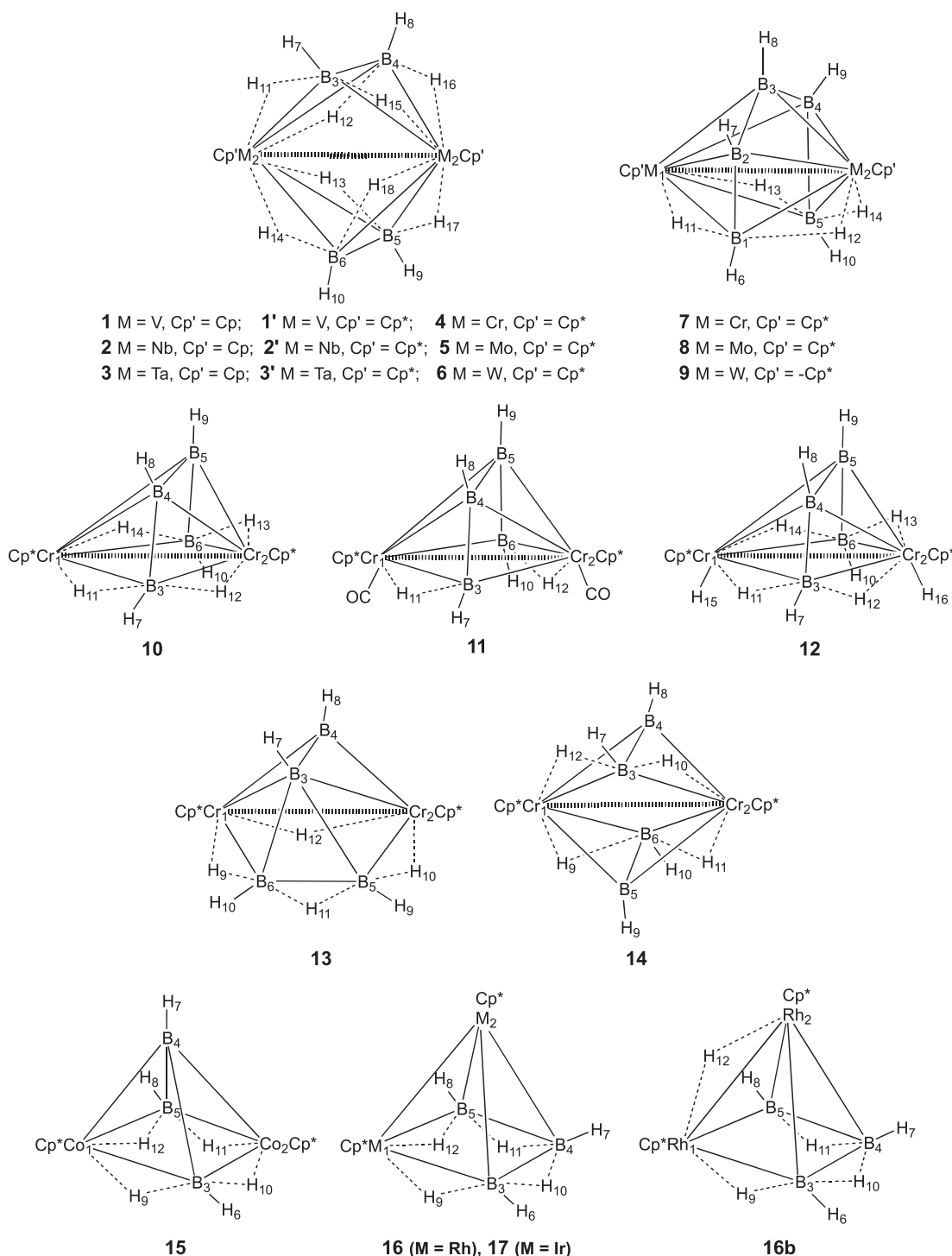


Chart 1. Examples of M_2B_3 , M_2B_4 and M_2B_5 dimetallaborane cluster compounds.

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