



Heterometallic boride clusters of group 6 and 9 transition metals



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ABSTRACT

Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with an *in-situ* generated intermediate, obtained from the reaction of $[\text{Cp}^*\text{MoCl}_4]$ and $[\text{LiBH}_4\cdot\text{THF}]$, led to the formation of $[\{\text{Cp}^*\text{Mo}(\text{CO})_2\}(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_3(\mu\text{-H})_2]$, **2** and $[\{\text{Cp}^*\text{Mo}(\text{CO})_2\}_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$, **3** ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). In a similar fashion, when $[\text{Ru}_3(\text{CO})_{12}]$ was thermalized with $[(\text{Cp}^*\text{Rh})_2\text{B}_2\text{H}_6]$, obtained from a fast metathesis reaction of $[\text{Cp}^*\text{RhCl}_2]_2$, **4** and $[\text{LiBH}_4\cdot\text{THF}]$, yielded a novel heterometallic boride cluster $[(\text{Cp}^*\text{Rh})_2(\mu_6\text{-B})\{\text{Ru}(\text{CO})_3\}_4\{\text{RuH}(\text{CO})_2\}]$, **5**. Both compounds **2** and **3** can be described as 50-cluster valence electron (cve) hetero-metallic boride clusters, in which the boron atom is in semi-interstitial position of a M_4 -butterfly geometry. Compound **5** contains 86 cluster valence-electrons, in which the boron atom is inside of an octahedral hole composed of one rhodium and five ruthenium atoms. Computational studies on the ground of density functional theory has been undertaken to analyze the bonding of **2**, **3** and **5**. The structural optimization yields geometries in agreement with the structure determinations and computed ^{11}B chemical shifts accurately reflect the observed shifts. The molecular orbital analysis of them shows that all the valence orbitals of boron have been participated in bonding and therefore provides the “encapsulation” picture of the boron atom. All the compounds have been characterized by IR and ^1H , ^{11}B , and ^{13}C NMR spectroscopy, and the geometries of the structures were unequivocally established by crystallographic analyses of compounds **2**, **3** and **5**.

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1. Introduction

Transition metal clusters that contain encapsulated elements constitute a substantial subsection of the chemistry of discrete and extended cluster systems [1]. In this context compounds containing main group element such as carbon, nitrogen and phosphorus at the interstitial environment are broadly studied [2,3]. The presence of the hetero-metal substantially perturbs the electron density of the main group element if the main-group atom is associated with the metal-cage, which in-turn reflects in their reactivity [4,5]. Metal borides are substances of considerable interest because of their physical, chemical, and electrical properties [6,7]. One of the characteristic features of the metal-boride clusters is the greater number of boron-to-metal contacts at the expense of boron-hydrogen bonds. Therefore, a true boride cluster contains a “naked” boron atom which is also deprived of hydrogen contacts. The familiar range of metal skeletons of various boride clusters is shown in Chart 1.

Over the past decade, our effort in synthesizing metallaboranes

using boranes and metal halides allowed us to isolate a variety of clusters with varying metal to boron ratio [8,9]. Cluster expansion reaction with metal carbonyls is also well studied and a combination of metal polychloride, borane and metal carbonyl fragments created interesting cluster geometries [10,11]. The reactions of transition metal fragment sources with metal clusters generally result in metal fragment substitutions or additions which can be rationalized on the ground of isolobal analogy [12]. In this report, we have studied the reactivity of molybdaboranes and rhodaboranes with $[\text{Ru}_3(\text{CO})_{12}]$, that yielded various boride clusters with $\mu_4\text{-B}$ and $\mu_6\text{-B}$ connectivity.

2. Results and discussion

As shown in Scheme 1, thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in toluene with an *in-situ* generated intermediate obtained from the treatment of $[\text{Cp}^*\text{MoCl}_4]$ with $[\text{LiBH}_4\cdot\text{THF}]$, led to the formation of **2** and **3**. On the other hand, reaction of a proposed intermediate $[(\text{Cp}^*\text{Rh})_2\text{B}_2\text{H}_6]$, obtained from a fast metathesis reaction of $[\text{Cp}^*\text{RhCl}_2]_2$, **4** and $[\text{LiBH}_4\cdot\text{THF}]$ with $[\text{Ru}_3(\text{CO})_{12}]$ yielded **5** (Scheme 2). Detailed spectroscopic and structural characterization of **2**, **3** and **5** using IR, ^1H , ^{11}B , ^{13}C NMR, mass spectrometry, and single crystal X-ray diffraction studies are discussed below.

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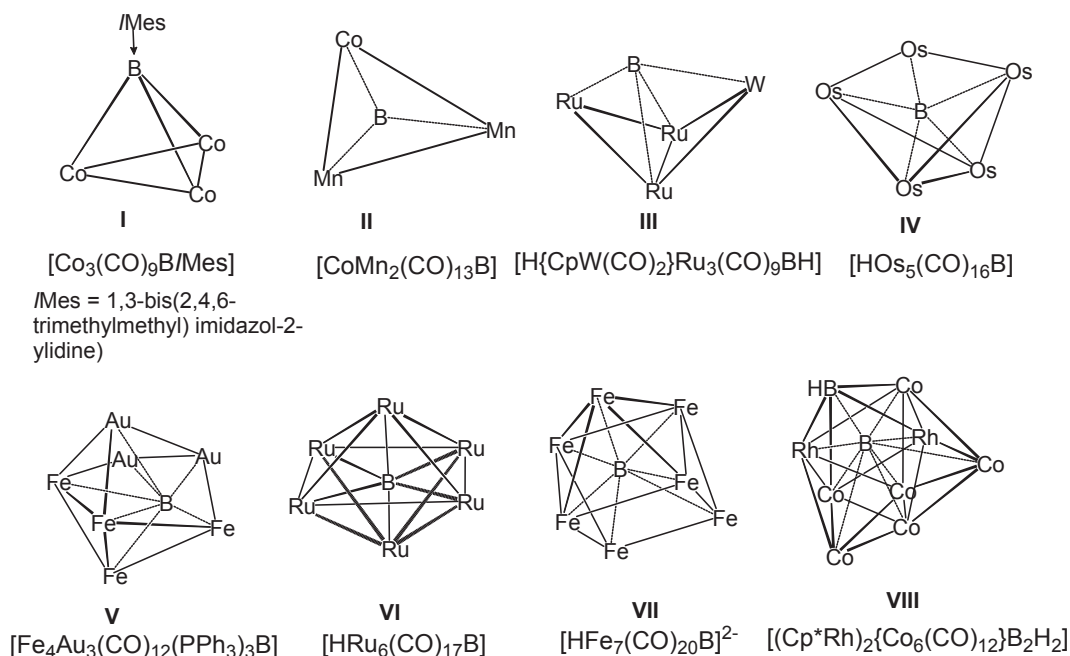
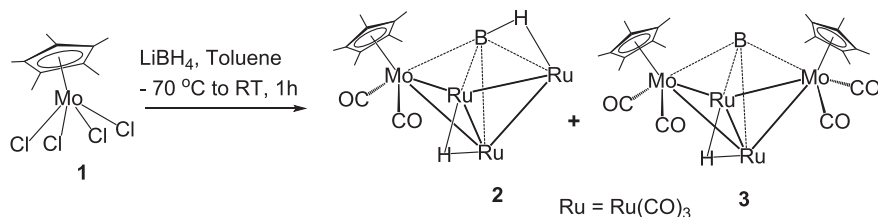
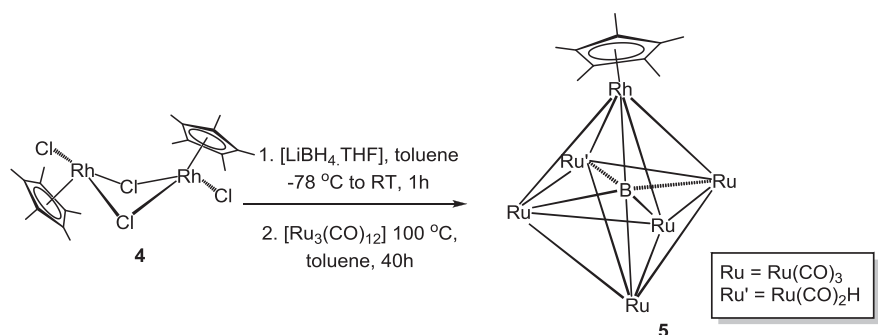


Chart 1. Different types of Transition Metal Boride Clusters (the ancillary ligands bound to metal centers are not shown for clarity).



Scheme 1. Synthesis of μ_4 -type boride clusters **2** and **3**.



Scheme 2. Synthesis of interstitial μ_6 -type heterometallic boride cluster **5**.

2.1. Synthesis and characterization of $[(\text{Cp}^*\text{Mo}(\text{CO})_2)(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_3(\mu\text{-H})_2]$, **2** and $[(\text{Cp}^*\text{Mo}(\text{CO})_2)_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$, **3**

Compounds **2** and **3** were isolated as moderately air stable orange and yellow solids, respectively. The room temperature ^{11}B NMR spectra of both **2** and **3** display single resonance in the down field region at $\delta = 123.1$ ppm and 128.4 ppm respectively. The ^1H NMR spectrum of **2** shows a single resonance for the Cp* protons and two up field chemical shift at $\delta = -5.5$ ppm and -18.8 ppm. Whereas, the ^1H NMR of **3** shows an up-field resonance at $\delta = -18.9$ ppm along with the signal for equivalent Cp* protons. The

occurrence of the CO ligands was confirmed by ^{13}C NMR and IR spectroscopy. The elemental analysis and mass spectrometric data suggests the formulation $[(\text{Cp}^*\text{Mo})\text{Ru}_3(\text{CO})_{11}\text{B}]$ for **2** and $[(\text{Cp}^*\text{Mo})_2\text{Ru}_2(\text{CO})_{10}\text{BH}]$ for **3**. However, evidence for the composition of **2** and **3** came from the single crystal X-ray crystallographic analysis (Fig. 1). Although the bridging hydride ligands of **2** were not located by X-ray, they were fixed on the basis of ^1H NMR spectrum.

Compound **2** crystallizes in monoclinic crystal system with $P2_1$ space group, whereas compound **3** crystallized in orthorhombic crystal system with Pcc_n space group. Compound **3** contains a

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