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Synthesis and structural characterization of group 5 dimetallaheteroboranes

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Dedicated to Professor V. I. Bregadze on the occasion of his 75th birthday.

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ABSTRACT

Treatment of group 5 metal polychlorides such as [Cp_nMCl_{4-x}] (M = Nb: $n = 1$, $x = 0$; M = V: n, $x = 2$), (Cp = η^5–C_5H_5) with [$LiBH_4 \cdot THF$] followed by thermolysis in presence of diphenyl dichalcogenide ligands, E_2Ph_2 (E = Se or Te) yielded dimetallaheteroborane clusters [$(CpNb)_2BH(Se)_4$], **1** and [$(CpV)_2B_3H_9(\mu_3\text{-}Te)$], **2** in modest yields. Compound **1** can be considered as an edge fused cluster in which a trigonal bipyramidal unit [Nb_2Se_2B] has been fused with a tetrahedral core [Nb_2Se_2] by means of a common [Nb_2] edge. Compound **2** can be described as a dimetallaheteroborane built from two edge-fused V_2B_2 tetrahedra, in which one of the BH_3 units is replaced by an isoelectronic Te ligand. All the compounds have been characterized by mass spectrometry, ^1H, ^{11}B, ^{13}C, ^{51}V and ^{77}Se NMR spectroscopy. In addition the geometry of compound **1** has been established by crystallographic analysis.

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1. Introduction

The metallacarborane cluster chemistry has been expanded very rapidly since the remarkable work on metallacarboranes by Hawthorne [1], Grimes [2,3] and others [4,5]. On the other hand, the chemistry of metallaborane has flourished since after the pioneer work of Felhner [6–13], and recently been finding applications in other areas of chemistry [14–16]. Our group has recently been interested in the synthesis and chemistry of the dimetallaheteroboranes of group 5, 6 and 8 transition metals [17–21] and reported a new class of dimetallaheteroborane clusters, such as [$(CpNb)_2B_4H_9(\mu\text{-}SePh)$] [17b], [$(CpNb)_2B_4H_{10}S$] [18] and [$(CpNb)_2B_4H_{11}S(^tBu)_2\text{-}C_6H_2OH$] [18] based on the reaction between [$CpNbCl_4$] with [$LiBH_4 \cdot THF$], followed by thermolysis in presence of various chalcogen sources. All these reactions also produced other products, which were observed during the chromatographic work up, however, because of their instability and insufficient amounts, isolation and characterization were not possible. It has been suggested that in most of the cases, the observed products distribution is due to the isoelectronic relation between BH_3 and S, Se or Te atoms. The use of heavier chalcogens, such as selenium and tellurium, has given rise to clusters with reactivity and structural patterns that are different from those of the sulfido clusters [22]. However, it is not clear that why there is a difference in reactivity pattern of these group 5 metal chlorides with various dichalcogenide ligands. As a result, we encouraged to investigate the chemistry of group 5 cyclopentadienylmetalchlorides with various dichalcogenide ligands. Herein, in this article, we report the results of the reactions of metal polychlorides with monoborane reagents in presence of dichalcogenide ligands, which afforded two novel dimetallaheteroborane clusters [$(CpNb)_2BH(Se)_4$], **1** and [$(CpV)_2B_3H_9(\mu_3\text{-}Te)$], **2**.

2. Results and discussion

2.1. Synthesis and characterization of compound 1

As shown in Scheme 1, reaction of [$CpNbCl_4$] with excess of $LiBH_4$ followed by pyrolysis in presence of [$BH_3 \cdot THF$] and diphenyl diselenide [Ph_2Se_2] yielded [$(CpNb)_2BH(Se)_4$] **1**, along with known [$(CpNb)_2B_4H_9(\mu\text{-}SePh)$] and [$(CpNbB_2H_6)$]$_2$ [17b]. Although compound **1** is produced in a mixture, this can be separated by

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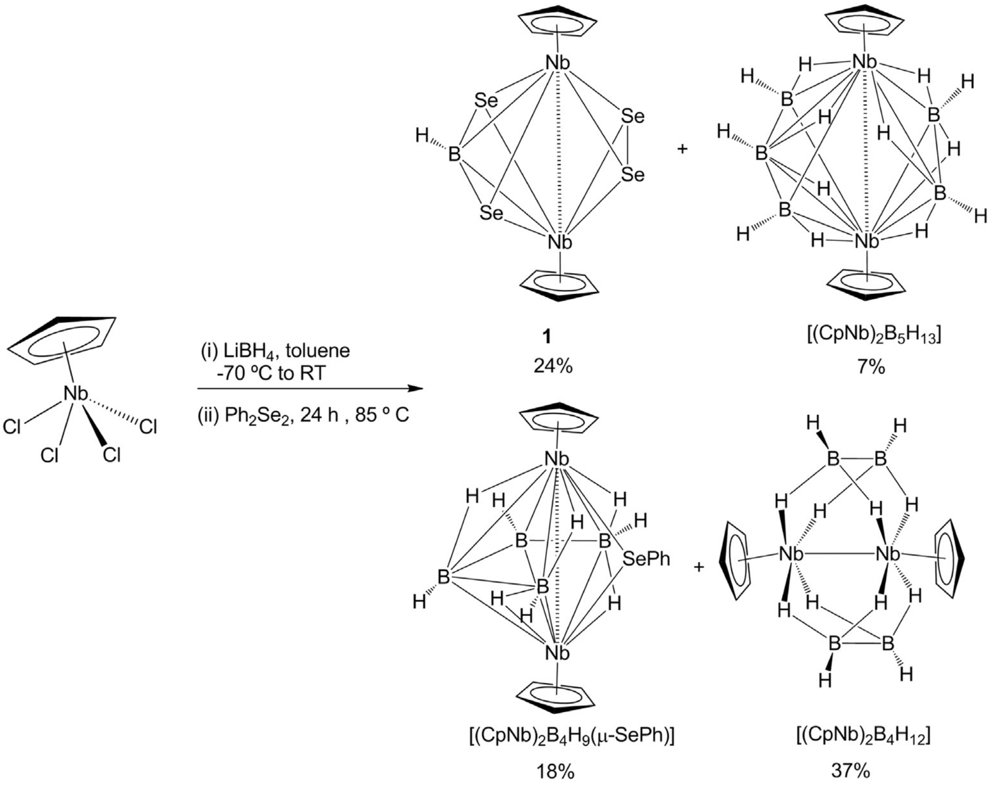

Scheme 1. Synthesis of [(CpNb)$_2$BH(Se)$_4$], **1**.

preparative thin-layer chromatography (TLC), allowing the characterization of pure materials. Cluster **1** was obtained in 24% yield by thermolysis at 85 °C for 24 h. The composition of **1** is defined by the FAB mass spectrometry. It shows a molecular ion peak at *m*/*z* 644 that corresponds to an isotopic distribution pattern characteristic of one boron, two niobium and four selenium atoms. The ^{11}B NMR of compound **1** displays a resonance at $\delta = -3.9$ ppm that predicts a probable attachment of a boron to selenium atom. The ^{1}H and ^{13}C NMR spectra imply two equivalents of Cp ligands. The ^{77}Se NMR of compound **1**, shown in Fig. 1, shows two chemical shifts each at $\delta = 330$ and 282 ppm comparable with other dimetallaselenaborane cluster [23]. The IR spectrum shows bands at 2510 cm^{-1}, owing to the terminal B–H bond. Therefore, from the mass spectral analysis combined with the ^{11}B, ^{1}H, ^{13}C and ^{77}Se NMR spectra, **1** is formulated as [{(η^5-C$_5$H$_5$)Nb}$_2$BH(Se)$_4$)]. The identity of **1** was not readily elucidated without the support of a crystal structure determination.

The crystals for X-ray analysis were obtained by slow evaporation of the hexane solution of **1**. The X-ray analysis showed that the asymmetric unit contains molecule **1** and an unknown molecule, proposed to be [(CpNb)$_2$B$_5$H$_{13}$]. The crystal selected for data collection was a co-crystal of two components namely **1** and the proposed [(CpNb)$_2$B$_5$H$_{13}$] with 50% occupancy (see Supplementary material for details). Physically it means that 50% of the molecular site in the crystal is occupied by **1** and other 50% by [(CpNb)$_2$B$_5$H$_{13}$] molecule. The view in Fig. 2 shows that the solid state structure of **1** can be described as edge fused cluster, generated from the fusion of

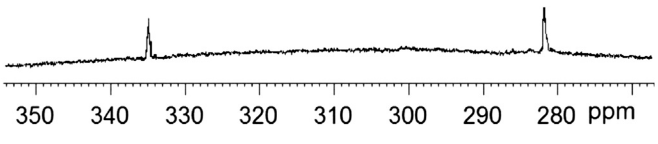

Fig. 1. ^{77}Se NMR chemical shifts of **1** (95.4 MHz, CDCl$_3$, 22 °C) spectrum.

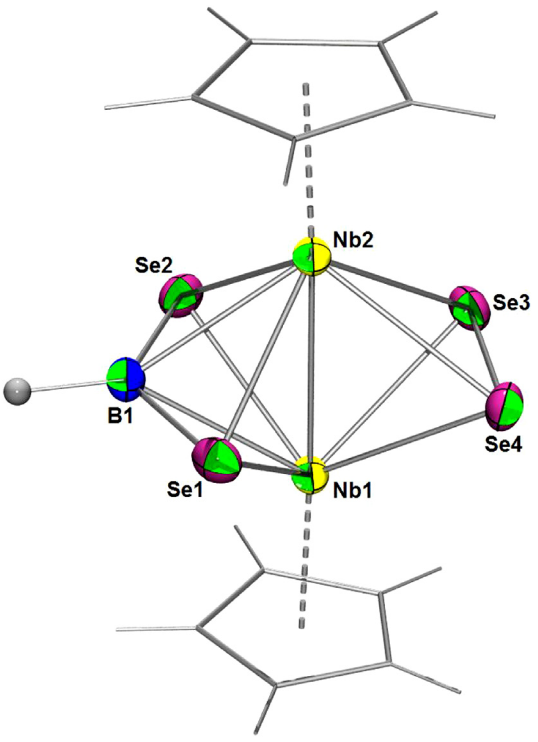

Fig. 2. X-ray structure of compound **1**. Selected bond lengths [Å] and bond angles (°): Se3-Se4 2.115(3), B1-Nb1 2.471(4), B1-Nb2 2.464(4), B1-Se1 1.886(5), B1-Se2 1.890(5), Se1-Nb1 2.5376(13), Se1-Nb2 2.5393(11), Se2-Nb2 2.5356(14), Se2-Nb1 2.5428(11); Se1-B1-Se2 130.5(2), Nb1-B1-Nb2 69.44(10), B1-Nb2-Se2 44.39(11), Se4 Se3 Nb1 66.44(7).

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