

Metallaheteroborane clusters of group 5 transition metals derived from dichalcogenide ligands

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ABSTRACT

Treatment of group 5 metal polychlorides such as, $[\text{Cp}_n\text{MCl}_{4-x}]$ ($\text{M} = \text{V}: n, x = 2$; $\text{M} = \text{Nb}: n = 1, x = 0$), or $[\text{Cp}^*\text{TaCl}_4]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), with $[\text{LiBH}_4 \cdot \text{THF}]$ followed by thermolysis in the presence of diphenyl diselenide yielded metallaheteroborane clusters $\{[\text{CpV}(\mu\text{-SePh})_2(\mu\text{-Se})]\}$, **1** $\{[\text{CpNb}]_2\text{B}_4\text{H}_9(\mu\text{-SePh})\}$, **2** and $\{[\text{Cp}^*\text{Ta}]_2\text{B}_4\text{H}_{11}(\text{SePh})\}$, **3** in modest yields. Compound **1** is an organovanadium selenolato cluster in which two (CpV) moieties bridged by ($\mu\text{-Se}$) and two ($\mu\text{-SePh}$) ligands. Compound **2** exhibits a bicapped tetrahedral core with one ($\mu\text{-SePh}$) ligand. **3** is a tantaloheteroborane cluster in which one of the terminal BH protons is substituted by SePh. Compounds **1–3** have been characterized by mass spectrometry, ^1H , ^{11}B , ^{13}C NMR spectroscopy, and the geometric structures were unequivocally established by crystallographic analysis of **1–3**.

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1. Introduction

The metallaborane chemistry [1–4], a part of inorganometallic chemistry [5], is concerned with compounds containing direct M–B bonding. There are now a large number of metallaboranes known [6,7], and both the electron-counting rules and the isolobal principle revealed interconnections between ostensibly unrelated molecules and defined the scope of the area [8,9]. On the other hand, the metallaheteroborane chemistry is extensive and has developed largely by the incorporation of one, two, or three atoms other than boron into the borane cluster. The conventional route to metallaheteroboranes proceeds in a sequence of steps leading from polyborane to heteroborane to metallaheteroborane [10]. Although there has been a resurgence of interest in such systems in recent years, there are very few examples in the literature, especially for the dimetallaheteroboranes of group 5 transition metals [4,6,11–13].

Part of our studies has focused on the syntheses and characterizations of novel metallaboranes of group 5–8 and their derivatives [12–15]. We have recently reported the reaction of $[\text{Cp}^*\text{MoCl}_4]$ with $[\text{LiBH}_4 \cdot \text{THF}]$ in presence of dichalcogenide ligands which yielded a new class of open-cage dimolybdaheteroborane clusters [13]. This reactivity prompted us to investigate the

chemistry of group 5 metal chlorides sources $[\text{Cp}^*\text{MCl}_n]$, ($\text{M} = \text{V}$, Nb, or Ta) with dichalcogenide ligands, for example diphenyl diselenide. The reaction can involve ligand exchange, ligand addition, or metal(s) incorporation either into the cage or as *exo*-polyhedral moieties [16]. Herein we report the results of the reactions of metal polychlorides with monoborane reagents in presence of diphenyl diselenide, which afforded dimetallaheteroboranes $\{[\text{CpV}(\mu\text{-SePh})_2(\mu\text{-Se})]\}$, **1**, $\{[\text{CpNb}]_2\text{B}_4\text{H}_9(\mu\text{-SePh})\}$, **2** and $\{[\text{Cp}^*\text{Ta}]_2\text{B}_4\text{H}_{11}(\text{-SePh})\}$, **3**.

2. Result and discussion

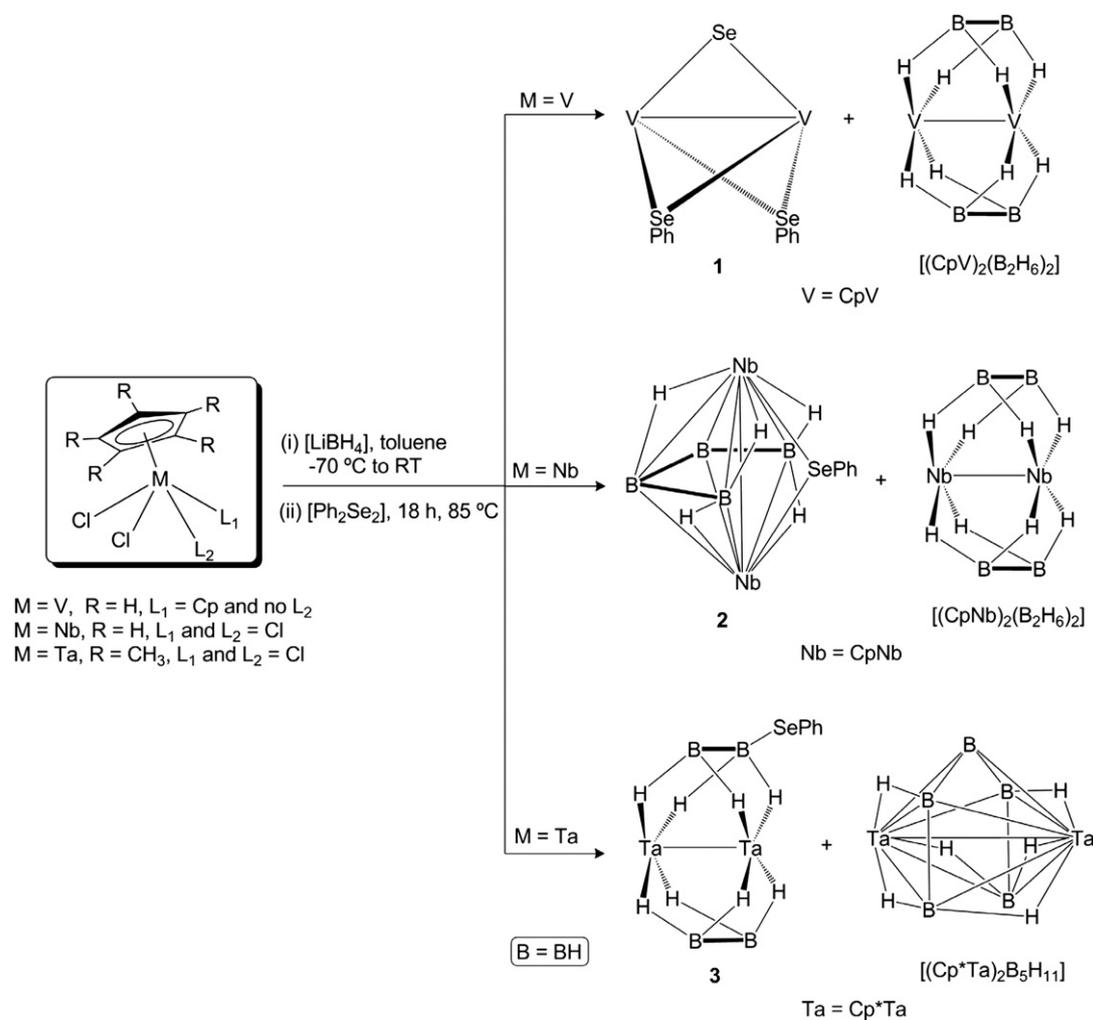
As shown in Scheme 1, reaction of $[\text{Cp}_n\text{MCl}_{4-x}]$ ($\text{M} = \text{V}: n, x = 2$; $\text{M} = \text{Nb}: n = 1, x = 0$) or $[\text{Cp}^*\text{TaCl}_4]$ with excess of $[\text{LiBH}_4 \cdot \text{THF}]$, followed by thermolysis in the presence of diphenyl diselenide (Ph_2Se_2) at 85 °C resulted **1**, **2** and **3**. In parallel with the formation of **1** and **2**, reaction of $[\text{Cp}_2\text{VCl}_2]$ and $[\text{CpNbCl}_4]$ yielded $\{[\text{CpV}]_2(\text{B}_2\text{H}_6)_2\}$ and $\{[\text{CpNb}]_2(\text{B}_2\text{H}_6)_2\}$ respectively [14b]. On the other hand, compound $[\text{Cp}^*\text{TaCl}_4]$ under the same reaction conditions, resulted in **3** and $\{[\text{Cp}^*\text{Ta}]_2\text{B}_5\text{H}_{11}\}$ [14a]. Details of spectroscopic and structural characterization of **1–3** are follows.

2.1. $\{[\text{CpV}(\mu\text{-SePh})_2(\mu\text{-Se})]\}$, **1**

Group 5 metal carbonyl compounds, such as $[\text{CpV}(\text{CO})_4]$, $[\text{Cp}^*\text{V}(\text{CO})_4]$ or $[\text{Cp}^*\text{Ta}(\text{CO})_4]$ are known to react with dichalcogenide

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Scheme 1. Synthesis of **1–3** (Cp and Cp* ligands are not shown for clarity).

ligands, of the type E_2R_2 or REH, ($E = S, Se, Te$; $R = Me, Ph$), to generate binuclear *bis*(organochalcogenolato)-bridged complexes $[CpM(CO)_2(\mu-ER)_2]$ and the non-carbonyl complexes $[CpM(\mu-ER)_2]_2$ ($M = V, Ta$; $E = S, Se, Te$) under vigorous conditions [17]. In contrast, $[Cp_2VCl_2]$ on reaction with Ph_2Se_2 yielded **1**, in parallel with the formation of $[(CpV)_2(B_2H_6)_2]$. The definitive assignment of the structure of **1** was obtained by X-ray crystallography. As shown in Fig. 1, two SePh moieties and one selenium (Se3) are bridged to two vanadium atoms of the VCp units. The μ -Se3 atom is disordered over two positions, each with an occupancy ratio of 2:1. Compound **1** is isostructural with the S analogue, $[(CpCr(\mu-SPh))_2(\mu-S)]$ [18]. Each vanadium atom in **1** is in an elongated tetrahedral coordination environment with the Cp ligand occupying the apical position and the two coordination polyhedra sharing a common basal plane comprising three bridging Se atoms.

The vanadium atoms V1 and V2 are joined by a V–V single bond (2.7435(6) Å). The dihedral angle between the planes of V1–Se1–V2 and V1–Se2–V2 is 97.7° . The mean V–Se(selenolato) bond distance (2.542 Å) is longer than the V–Se(selenido) bond distance of 2.404 Å in $[(Cp^*V)_2(\mu-\eta^1-Se_2)(\mu-S)_2]$ [19]. Selenium-carbon(phenyl) distances of 1.938(3) and 1.939(3) Å, compare favorably with other Se–C distances, e.g., 1.935 Å in $[(CO)_3Mn(\mu-SePh)_3Fe(CO)_3]$ [20]. The two cyclopentadienyl ligands are approximately in an eclipsed configuration about the V1–V2 bond, and the dihedral angle between their least-squares planes is 6.70° .

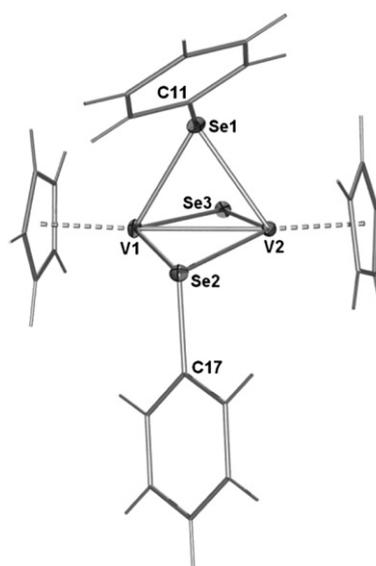


Fig. 1. Molecular structure and labeling diagram for **1**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles ($^\circ$): V(1)–V(2) 2.7435(6), V(1)–Se(1) 2.5446(5), V(2)–Se(1) 2.5294(5), V(1)–Se(3) 2.4937(5), V(2)–Se(3) 2.4948(5); V(1)–Se(1)–V(2) 65.461(14), V(1)–Se(2)–V(2) 65.151(15), V(1)–Se(3)–V(3) 66.729(16).

Table 1
Characteristic structural and spectroscopic data of **1** and the other binuclear complexes.

Complex	$d[M-M]$ [Å]	$d[E\cdots E]$ [Å] ^a	Angle [°] V–E–V	Dihedral angles [°]		⁵¹ V NMR [ppm]
				at E⋯E	at V⋯V	
[Cp ⁺ V(CO) ₂ (μ-SPh)] ₂	3.07	2.78	77.7, 77.7	80.7	93.6	–686
[(CpV(μ-SePh)) ₂ (μ-Se)] 1	2.74	3.22	65.4, 65.1, 66.7	97.7 ^b	91.5	–644
[Cp ⁺ V(CO) ₂ (μ-TePh)] ₂	3.29	3.19	74.5, 73.5	84.3	86.1	–804

^a E = S, Se, Te.

^b Dihedral angles at Se(Ph)⋯Se(Ph).

Consistent with the X-ray results, the ¹H NMR spectrum of **1** suggests the structure, if static, of higher symmetry. The NMR spectra of **1** did not give any indications of the existence of isomers in solution; only one signal was found for two Cp ligands. The ⁷⁷Se NMR of **1** shows two resonances, one at δ 557 ppm for the bridged μ-SePh and another downfield resonance at δ 671 ppm for the μ-Se atom. The ⁵¹V chemical shift of the binuclear complex **1** is observed at δ –644 ppm, which is comparable with those of other binuclear vanadium complexes, [CpV(CO)₂(μ-ER)]₂ and [Cp⁺V(CO)₂(μ-ER)]₂ (E = S, Se; R = Me, Ph) (Table 1) [21].

2.2. [(CpNb)₂B₄H₉(μ-SePh)], **2**

Compound **2** was isolated as a green, relatively air-stable solid. The molecular ion peak in the FAB mass spectrum corresponds to [(CpNb)₂B₄H₉(SePh)]. The IR spectrum of **2** features strong bands at 2466 and 2418 cm^{–1}, owing to the terminal B–H stretches. The ¹¹B NMR spectrum of **2** rationalizes the presence of four ¹¹B resonances with an equal intensity. Besides the BH terminal and Nb–H–B protons, the ¹H NMR spectrum implies one equivalent of Cp ligands. The ¹³C NMR spectrum of **2** shows four resonances, which are assigned to the Cp ligands and to the phenyl carbon atoms. The ⁷⁷Se NMR shows single resonance at δ 533 ppm that is comparable with the dimolybdaheteroborane cluster [(Cp⁺Mo)₂B₄H₉(μ-Seph)] [13].

In order to confirm the spectroscopic assignments and determine the full molecular and crystal structure of **2** an X-ray analysis was undertaken. Suitable crystals were obtained from a solution in hexane/dichloromethane (9:1) at –10 °C. The molecular structure of **2**, shown in Fig. 2, contains a bicapped tetrahedral geometry of [(CpNb)₂B₄H₉] with a μ-SePh group bridging two Nb atoms of the central tetrahedron. Based on the capping principle the skeletal electron count is determined by the central polyhedron, i.e. the M₂B₂ tetrahedron, and is six skeletal electron pairs (sep) [9]. Formally, μ-SePh group contributes three electrons; hence for **2**, six sep is available and the observed structure obeys the counting rules [8,9].

The Nb–Nb distance of 2.8618(5) Å in **2** is comparable with Nb–Nb distances in niobium metal (2.858 Å), however shorter than those observed in dinuclear niobium complexes [Nb₂Se₄][Te₂I₆]₂ (2.926(2) Å) [22], [Nb₂(μ-S₂)₂(H₂O)₈](pts)₄·4H₂O (2.8984(7) Å; Hpts = *p*-toluenesulfonic acid) [23] and [Nb₂(μ-Se₂)₂(dte)₄] (2.974(2) Å; dte = diethyldithiocarbamate) [24]. The average bridging Nb–Se distance (2.6992 Å) in **2** is about 0.06 Å longer than that observed in [Nb₂Se₄(Et₂NCS₂)₄] (2.6392 Å) [24]. The average Nb–B distance of 2.386 Å lies in the range of those reported for the niobium boron complexes [25]. The angle between the wings of the Nb₂B₂ “butterfly” of 163.74° is comparable to the related cluster [(Cp⁺Mo)₂B₄H₉(μ-Seph)] [13]. The Cp ligands, bonded to the niobium centers, are tilted from the mean plane of the four boron and one selenium atom such that the dihedral angles between them are 3.67° and 7.00°.

All the five Nb–H–B bridging hydrogen atoms of molecule **2** have not been positioned by X-ray diffraction studies, however their connectivity, both with metal and boron atoms (Scheme 1),

have indubitably been located by low temperature ¹H{¹¹B} NMR spectra (Fig. 3). At room temperature the ¹H{¹¹B} NMR of compound **2** shows single resonance at δ –8.55 ppm corresponds to five Nb–H–B protons. Upon lowering the temperature to –60 °C, the resonance at δ –8.55 ppm splits into three distinct peaks (δ –8.58, –8.60 and –16.75 ppm) in a 2:2:1 ratio. This evidently implies that three resonances merged into a single broad peak at δ –8.55 ppm at room temperature. Based upon the pattern of assembly of peaks for the bridging protons in ¹H NMR spectra, the resonances at δ –8.58 and –8.60 ppm have been assigned to those which bridge the open face of boron atoms. The resonance at δ –16.75 ppm has been assigned to the proton which is bonded to the tetrahedral core (Nb–H–B₂ or Nb–H–B₃). Similarly, at low temperature the Cp protons at δ 6.05 ppm splits into two peaks at δ 6.11 and 6.04 ppm with a relative intensity of 5:5. The above results demonstrate that at the lowest experimental temperatures, both Nb1 and Nb2 become inequivalent owing to the asymmetric arrangements of the bridging H atoms.

Comparison of the structural parameters and chemical shift of **2** with those of Cr [26], Re [27], Ta [14a] and Mo analogues [13], reveals several contrasting features (Table 2). Although, the M–M distance in **2** is comparable, the average M–B distances are markedly longer. The distance between the two capping boron atoms differ to some extent with respect to the size of the open face of the

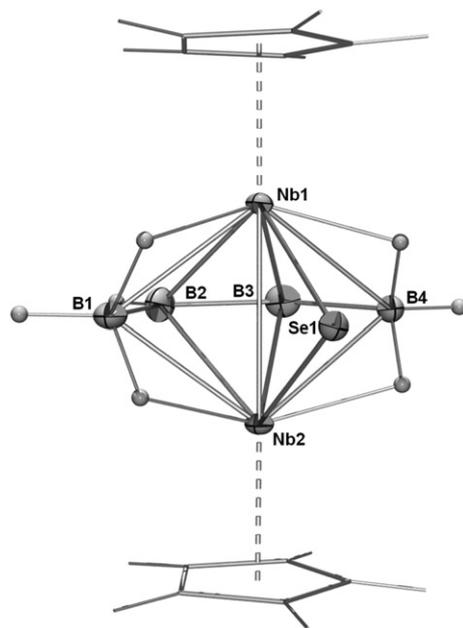


Fig. 2. Molecular structure and labeling diagram for **2**. Phenyl group is not shown for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Nb(1)–Nb(2) 2.8618(5), Nb(1)–B(1) 2.406(6), Nb(1)–Se(1) 2.7022(6), Nb(2)–Se(1) 2.6962(6), Nb(2)–B(1) 2.403(6), B(1)–B(2) 1.779(9), B(2)–B(3) 1.727(8); B(1)–B(2)–B(3) 126.0(4), B(2)–Nb(1)–B(1) 43.9(2), Nb(2)–B(1)–Nb(1) 67.8(3), Nb(1)–Se(1)–Nb(2) 64.026(15).

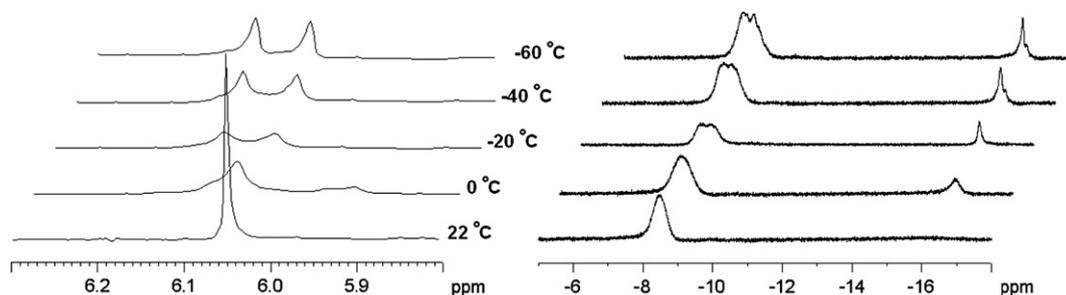


Fig. 3. Variable-temperature $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of **2** in $[\text{D}_8]$ toluene with the $-60\text{ }^\circ\text{C}$ spectrum at the top and the $22\text{ }^\circ\text{C}$ spectrum at the bottom.

Table 2

Selected structural parameters and spectroscopic data of **2** and other related compounds.

Compound	Sep	$d[\text{M}-\text{M}]$ [Å]	Avg. $d[\text{M}-\text{B}]$ [Å]	$d[\text{B}\cdots\text{B}]^a$ [Å]	Dihedral angle $[\text{ }^\circ]^b$	^{11}B NMR [ppm]
$[(\text{Cp}^*\text{Cr})_2\text{B}_4\text{H}_8]$	5	2.87	2.06	3.02	147.6	34.3, 126.5
$[(\text{Cp}^*\text{ReH}_2)_2\text{B}_4\text{H}_4]$	6	2.81	2.17	3.20	163.4	1.30, 68.7
$[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{10}]$	5	2.89	2.38	3.74	167.7	0.3, 16.6
$[(\text{Cp}^*\text{Mo})_2\text{B}_2\text{H}_5(\text{B}-\text{SePh})_2(\mu-\text{SePh})]$	6	2.70	2.27	3.69	168.0	78.8, 54.0, 19.2
2	6	2.86	2.38	3.82	163.7	18.2, 15.1, 3.0, -0.2

^a Distance between two capped borons (B_1 and B_4) in the open face of bicapped tetrahedral geometry.

^b Dihedral angle of M_2B_2 tetrahedral geometry.

cluster, which is more open in **2**. The ^{11}B resonances, on going from the lighter to the heavier metal atom, appeared at high field. As the qualitative cluster shapes of **2** and $[(\text{Cp}^*\text{Mo})_2\text{B}_2\text{H}_5(\text{BSePh})_2(\mu-\eta^1-\text{SePh})]$ same, differences are sought in the magnitude of the structural parameters due to the perturbation of the electronic environment of the boron atoms as well as the positioning of the hydrogen atoms.

2.3. $[(\text{Cp}^*\text{Ta})_2\text{B}_4\text{H}_{11}(\text{SePh})]$, **3**

The reaction of diphenyl diselenide with an in situ generated intermediate, produced from the reaction between $[\text{Cp}^*\text{TaCl}_4]$ and $[\text{LiBH}_4\cdot\text{THF}]$, has been investigated. The objective of generating metallaheteroborane clusters was not achieved, however, new cage substituted metallaborane **3** was isolated along with tantalaborane complex $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$ [**14a**]. The composition of **3** is recognized from the elemental analysis together with multinuclear NMR spectroscopy. The ^{11}B NMR spectrum of **3** exhibits three signals at δ 0.1, -3.3 and -8.0 ppm with 1:2:1 ratio. The chemical shift at δ -8.0 ppm is assigned to the B–SePh as it remained a singlet in

coupled ^{11}B spectrum, whereas the other peaks became doublet. The $^1\text{H}\{^{11}\text{B}\}$ spectrum suggests the presence of two kind of terminal H atoms and three kind of bridging H atoms, at δ -9.4 , -10.5 and -10.9 ppm with 1:2:1 intensity ratio. The ^{77}Se NMR of **3** shows single resonance at δ 573 ppm for the cage B–SePh group.

The molecular structure of **3**, shown in Fig. 4, is consistent with the analysis of the observed spectroscopic data and reveals core geometry that is the same as that observed for $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)_2]$ [**14b**]. The Ta–B bond lengths of **3** ranges from 2.36 Å to 2.41 Å and are similar to that observed for $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)_2]$. The B–B distances in **3** range from 1.75 Å to 1.80 Å is in the range expected for the directly bonded ethane-like $(\text{BH}_3-\text{BH}_3)^{2-}$ ligand, however, markedly shorter than that observed for the hydrogen-bridged $(\text{H}_2\text{BHBH}_3)^{2-}$ ligand in $[(\text{Cp}^*\text{TaBr})_2\text{B}_2\text{H}_6]$ (1.88(3) Å) [28]. The B–Se distance (2.046(9) Å) is longer comparable to that observed in $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{Se}_2]$ [12b]. However, they are significantly shorter when compared to those observed in other selenaborane clusters [29]. This may be due to the tendency of the boron and selenium atoms to form polarized bonds that have a localized two-center character resulting in the observed distances [30]. The bond angle of the B–Se–C moiety ($104.7(4)^\circ$) in **3** suggests that the selenium atom is in sp^3 hybridization.

3. Conclusions

We have established the synthesis of group 5 organoselenolato-bridged complex, **1** and two metallaheteroborane compounds **2** and **3**, from the reaction of metal polychlorides with $[\text{LiBH}_4\cdot\text{THF}]$ and Ph_2Se_2 . The difference in reactivity pattern of the group 5 metal chlorides with dichalcogenide ligand is also reflected in the observed product distribution. Apparently, these results highlight the possibility of the synthesis of a new class of metallaheteroborane clusters.

4. Experimental

4.1. General procedures and instrumentation

All the operations were conducted under an Ar/ N_2 atmosphere using standard Schlenk techniques or glove box. Solvents were

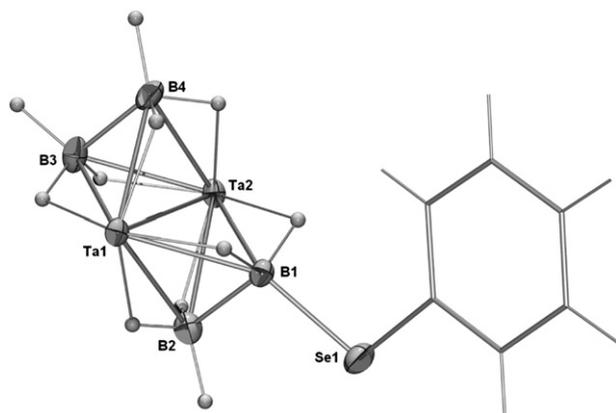


Fig. 4. Molecular structure and labeling diagram for **3**. Cp* ligands are not shown for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ta(1)–Ta(2) 2.9454(5), Ta(1)–B(1) 2.368(9), Ta(2)–B(1) 2.382(9), Ta(1)–B(2) 2.413(10), Ta(2)–B(2) 2.379(11), B(1)–B(2) 1.757(13), B(3)–B(4) 1.800(15), B(1)–Se(1) 2.046(9); Ta(1)–B(1)–Ta(2) 76.6(3), Ta(1)–B(2)–Ta(2) 75.8(3), Ta(1)–B(3)–Ta(2) 76.8(3), C(21)–Se(1)–B(1) $104.7(4)$.

distilled prior to use under Argon. $[(\text{Cp})_2\text{VCl}_2]$, $[\text{CpNbCl}_4]$, $[\text{Cp}^*\text{TaCl}_4]$ and $[\text{LiBH}_4 \cdot \text{THF}]$ were used as received (Aldrich). $[\text{Ph}_2\text{Se}_2]$ [31] was prepared as described in literature. The external reference $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$, for the ^{11}B NMR, was synthesized with the literature method [32]. ^{51}V NMR spectrum was recorded on 400 MHz Bruker FT-NMR spectrometer operating at 105 MHz (^{51}V) and chemical shifts are in parts per million relative to a VOCl_3 external reference. Thin layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26), while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in $[\text{D}_6]$ benzene (δ_{B} , ppm, -30.07) was used as an external reference for the ^{11}B NMR. Microanalyses for C and H were performed on Perkin Elmer Instruments series II model 2400. Infrared spectra were recorded on a Nicolet 6700 FT spectrometer. Mass spectra were obtained on ESI Q-ToF Micro mass Spectrometer and Jeol SX 102/Da-600 mass spectrometer/data system using Argon/Xenon (6 kv, 10 mA) as the FAB gas.

4.2. General synthesis of 1–3

In a typical reaction, $[\text{Cp}_2\text{VCl}_2]$ (0.08 g, 0.32 mmol) was loaded in toluene (12 mL) and cooled to -70°C , $[\text{LiBH}_4 \cdot \text{THF}]$ (1.0 mL, 1.92 mmol) was added via syringe and the reaction mixture was allowed to warm slowly to room temperature and left stirring for an additional hour. The solvent was evaporated under vacuum, the residue was extracted into hexane and filtration afforded an extremely air and moisture-sensitive red-blue intermediate. The filtrate was concentrated and a toluene solution (15 mL) of the intermediate was thermolyzed at 85°C with excess of Ph_2Se_2 (0.2 g, 0.64 mmol) for 18 h. The solvent was dried and the residue was extracted into hexane and passed through Celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/ CH_2Cl_2 (90:10 v/v) mixture yielded air-stable red orange **1** (0.03 g, 15%). Under same reaction conditions green **2** (0.03 g, 21%) and purple **3** (0.04 g, 27%) were isolated from the reaction of Ph_2Se_2 with $[\text{CpNbCl}_4]$ and $[\text{Cp}^*\text{TaCl}_4]$ respectively.

Note that compounds **1–3** have been isolated along with the metallaborane $[(\text{CpM})_2(\text{B}_2\text{H}_6)_2]$ ($\text{M} = \text{V}, \text{Nb}$) and $[(\text{Cp}^*\text{Ta})_2\text{B}_5\text{H}_{11}]$ respectively reported earlier [14a,b].

1: ^{51}V NMR (105 MHz, CDCl_3 , 22°C): δ -644.0 (s, br, 2 V); ^1H NMR (400 MHz, CDCl_3 , 22°C): δ 7.78–6.86 (m, 10H, $2\text{C}_6\text{H}_5$), 5.96 (s, 10H; 2Cp); ^{13}C NMR (100 MHz, CDCl_3 , 22°C): δ 134.0, 126.4, 125.3 (s, C_6H_5), 98.6 (s; C_5H_5); ^{77}Se NMR (95.38 MHz, CDCl_3 , 22°C): δ 671 (s, Se), 557 (s, 2SePh); MS (ESI $^+$): m/z (%) = 623 $[\text{M}]^+$; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{20}\text{Se}_3\text{V}_2$: C 42.40, H 3.23; found: C 41.68, H 3.06.

2: ^{11}B NMR (128 MHz, CDCl_3 , 22°C): δ 18.2 (br, 1B), 15.1 (br, 1B), 3.0 (br, 1B), -0.2 (br, 1B); ^1H NMR (400 MHz, CDCl_3 , 22°C): δ 7.48–6.78 (m, 5H; C_6H_5), 6.04 (s, 10H; 2Cp), 4.58 (partially collapsed quartet (pcq), 1BH_t), 4.34 (pcq, 1BH_t), 2.01 (pcq, 1BH_t), 1.28 (pcq, 1BH_t), -8.55 (br, 5Nb-H-B); ^{13}C NMR (100 MHz, CDCl_3 , 22°C): δ 134.1, 127.8, 126.4, 124.6 (C_6H_5), 97.5 (s; C_5H_5); ^{77}Se NMR (95.38 MHz, CDCl_3 , 22°C): δ 533 (s, Se), IR (hexane): ν_{bar} = 2466 and 2418 cm^{-1} (BH_t); MS (FAB) P^+ (max): m/z (%): 524 (isotopic pattern for 2Nb, 4B and 1Se atoms); elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{24}\text{B}_4\text{Nb}_2\text{Se}_1$: C 36.65, H 4.61; found: C 35.79, H 4.11.

3: ^{11}B NMR (128 MHz, CDCl_3 , 22°C): δ 0.1 (s, br, 1B; BH), -3.3 (d, 2B; BH), -8.0 (d, 1B); ^1H NMR (400 MHz, CDCl_3 , 22°C): δ 7.78–7.45 (m, 5H; C_6H_5), 3.91 (pcq, 1BH_t), 3.62 (pcq, 2BH_t), 2.36 (s, 30H, 2Cp^*), -9.41 (br, 2Ta-H-B), -10.52 (br, 4Ta-H-B), -10.90 (br, 2Ta-H-B); ^{13}C NMR (100 MHz, CDCl_3 , 22°C): δ 129.0, 128.5, 127.5, 127.1 (C_6H_5), 109.4 (s; C_5Me_5), 12.9 (s, C_5Me_5); ^{77}Se NMR (95.38 MHz,

CDCl_3 , 22°C): δ 573 (s, Se); IR (hexane): ν_{bar} = 2456 cm^{-1} (BH_t); elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{46}\text{B}_4\text{Se}_1\text{Ta}_2$: C 37.05, H 5.50; found: C 38.41, H 5.20.

4.3. X-ray structure determination

Crystal data for **1** and **3** were collected and integrated using OXFORD DIFFRACTION XALIBUR-S CCD system equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) radiation at 150 K. Crystal data **2** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite-monochromated Mo- $K\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation at 173 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 [33] and refined using SHELXL-97 (Sheldrick, G.M., University of Göttingen) [34,35].

Crystal data for **1**: CCDC 819252, Formula, $\text{C}_{22}\text{H}_{20}\text{Se}_3\text{V}_2$; Formula weight, 623.14 g/mol; Crystal system, space group: monoclinic, $\text{P}2_1/\text{c}$. Unit cell dimensions, $a = 15.2867(3)$, $b = 8.29110(10)$, $c = 18.4289(4)\text{ \AA}$, $\beta = 110.210(2)^\circ$; $Z = 4$. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0268$, $wR^2 = 0.0703$. Index ranges $-21 \leq h \leq 20$, $-11 \leq k \leq 11$, $-21 \leq l \leq 25$. θ range for data collection $3.26\text{--}30.00^\circ$. Crystal size $0.33 \times 0.28 \times 0.21\text{ mm}^3$. Density (calculated) 1.888 Mg/m^3 . Reflections collected 22896, independent reflections 6394 $[R(\text{int}) = 0.0295]$, Goodness-of-fit on F^2 0.956.

Crystal data for **2**: CCDC 819250, Formula, $\text{C}_{16}\text{H}_{23}\text{B}_4\text{Nb}_2\text{Se} \cdot \text{CH}_2\text{Cl}_2$; Formula weight, 608.29 g/mol; Crystal system, space group: Triclinic, $\text{P}-1$. Unit cell dimensions, $a = 9.9310(4)$, $b = 10.5787(5)$, $c = 11.0913(5)\text{ \AA}$, $\alpha = 79.902(2)$, $\beta = 72.534(2)$, $\gamma = 88.369(2)^\circ$; $Z = 2$. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0381$, $wR^2 = 0.0818$. Index ranges $-13 \leq h \leq 12$, $-10 \leq k \leq 14$, $-11 \leq l \leq 14$. θ range for data collection $1.95\text{--}28.40^\circ$. Crystal size $0.23 \times 0.20 \times 0.10\text{ mm}^3$. Density (calculated) 1.847 Mg/m^3 . Reflections collected 14533, independent reflections 5141 $[R(\text{int}) = 0.0274]$, Goodness-of-fit on F^2 1.040.

Crystal data for **3**: CCDC 819249, Formula, $\text{C}_{26}\text{H}_{46}\text{B}_4\text{SeTa}_2$; Formula weight, 842.73 g/mol; Crystal system, space group: monoclinic, $\text{P}2_1/\text{c}$. Unit cell dimensions, $a = 11.7339(3)$, $b = 10.0150(3)$, $c = 25.4381(10)\text{ \AA}$, $\beta = 98.074(3)^\circ$; $Z = 4$. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0463$, $wR^2 = 0.1128$. Index ranges $-15 \leq h \leq 15$, $-13 \leq k \leq 12$, $-33 \leq l \leq 33$. θ range for data collection $3.26\text{--}27.50^\circ$. Crystal size $0.28 \times 0.23 \times 0.22\text{ mm}^3$. Density (calculated) 1.891 Mg/m^3 . Reflections collected 23773, independent reflections 6747 $[R(\text{int}) = 0.0821]$, Goodness-of-fit on F^2 0.965.

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Appendix A. Supplementary material

CCDC 819249, 819250 and 819252 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.jorganchem.2011.06.040.

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