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Chemistry of Vanadaboranes: Synthesis, Structures, and Characterization of Organovanadium Sulfide Clusters with Disulfido Linkage

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Vanadaborane, $[(CpV)_2(B_2H_6)_2]$ (Cp = η^5-C_5H_5), **1** reacts with elemental sulfur to afford the hexasulfide cluster $[(CpV)_2S_4(\mu$-η^1-$S_2)]$, **2** in high yield. Compound **2** is a notable example of an organovanadium sulfide cluster in which the $[V_2S_4]$ atoms define a bicapped tetrahedron framework, with one μ-η^1-S_2 ligand bridged the two (CpV) moieties. The sulfur atom in $[V_2S_4]$ core in **2** is a four-skeletal-electron donor isoelectronic with the BH_3 unit; therefore, the replacement of boron hydride in **1** by four sulfur atoms necessitates the formation of a bicapped tetrahedron $[V_2S_4]$ framework. Furthermore, this is the only reported example of a bimetallic hexasulfide cluster containing vanadium. Pyrolysis of **1** with *bis*-chalcogenide ligands such as Ph_2S_2 and Bz_2Se_2 (Bz = $PhCH_2$), results in the formation of substituted vanadahexaboranes $[(CpV)_2B_4H_{12-x}L_x]$, **3**–**5** (**3**: L = SPh: $x = 3$; **4**: L = SPh, $x = 2$; **5**: L = SeBz: $x = 1$) in modest yield. All these new compounds have been characterized by mass, ^{1}H, ^{11}B, ^{13}C NMR spectroscopy, and elemental analysis, and the structural types were unequivocally established by crystallographic analysis of compounds **2**–**5**.

Introduction

The chemistry of transition metal complexes with chalcogen ligands is of immense importance to a wide range of chemical, industrial, and biological systems.[1-12] These complexes have also been used as molecular precursors for the preparation of advanced materials[13] and industrial catalysis.[14] Extensive studies have documented the reactivity associated with the chalcogenide ligands in discrete metal sulfido complexes.[15-21] For example, compounds of the type $[(RC_5H_4)_2TiS_5]$ (R = H, CH_3), $[(RC_5H_4)_2V_2S_4]$ (R = H, CH_3, $(CH_3)_2CH$), $[(Cp_2Cr_2S(S$-t-$Bu)_2]$, $[(CH_3R_4C_5)_2Mo_2S_4]$ (R = CH_3, H) and $[Fe_2(S_2)(CO)_6]$ have been employed for organic

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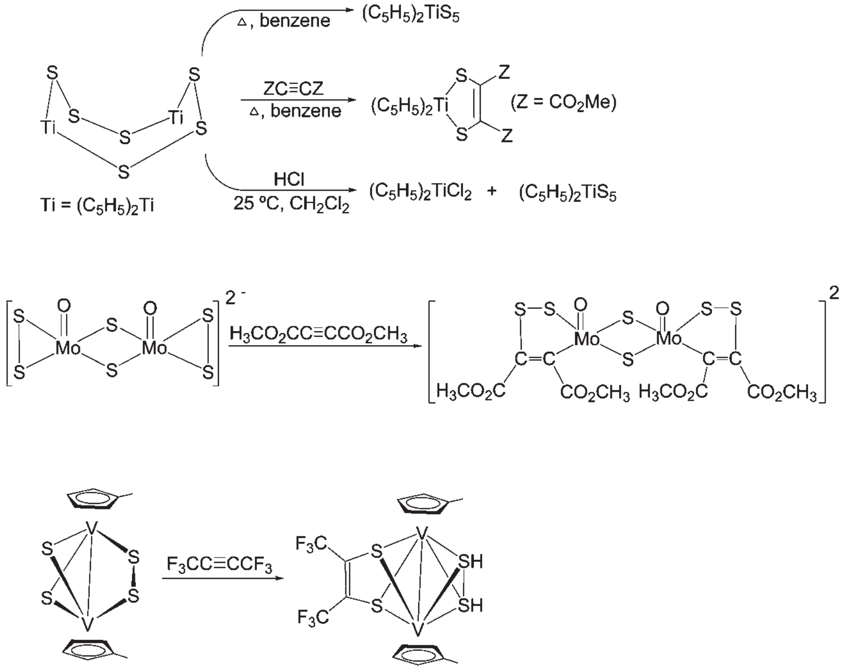
Chart 1. Reactivity of Chalcogenide Ligands in Discrete Metal Sulfido Complexes



synthesis, for the assembly of unusual mixed-metal clusters, and as hydrogenation catalysts (Chart 1).[22]

On the other hand, the metallaborane chemistry is an interesting and diverse area of cluster chemistry which is closely allied to both polyhedral metal compounds as well as boron hydrides.[23−27] Some of them are isoelectronic with metal-hydrocarbyl complexes of organometallic chemistry,[26] and some display unprecedented cluster shapes that reveal unique properties of compounds containing direct transition metal−boron bonds.[24b,27] In contrast to organometallic chemistry, our knowledge of the characteristic reactivities associated with metallaboranes of the early transition metals is in a fundamental state. We have recently synthesized a series of low boron content metallaboranes containing a range of early transition metal atoms, $[(CpM)_2(B_2H_6)_2]$ (M = V, Nb) and $[(Cp^*Ta)_2(B_2H_6)_2]$ ($Cp^* = \eta^5$-C_5Me_5), by the reaction of metal polychlorides (V, Nb, and Ta) with monoborane reagents ($LiBH_4 \cdot thf$ or $BH_3 \cdot thf$) in high yield.[28,29] The present report is concerned with the reactivity of one of these compounds, $[(CpV)_2(B_2H_6)_2]$, **1**, with elemental sulfur and *bis*-chalcogenide ligands. The work has yielded unexpected products in terms of the reactions that occur when **1** interacts with elemental sulfur and *bis*-chalcogenide ligands. Reported here are the synthesis, structural characterization, and bonding of the organovanadium sulfide cluster $[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$, **2**, and substituted vanadahexaborane clusters $[(CpV)_2B_4H_{12-x}L_x]$, **3**−**5** (**3**: L = SPh: $x = 3$; **4**: L = SPh, $x = 2$; **5**: L = SeBz: $x = 1$).

Results and Discussion

Formation and Properties of $[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$ (2). After it had been revealed that the pyrolysis of stable diboranato complex, $[(\eta^5\text{-}C_5Me_4EtNb)_2(B_2H_6)_2]$, with sulfur yielded $[(\eta^5\text{-}C_5Me_4EtNb)_3BHS_7]$ in moderate yield,[30] an investigation of a related vanadium system became of interest. As the results obtained with the niobium complex suggested that a tetrathioborate complex now be accessible, we pursued this chemistry in a vanadium system. Although the objective of generating a tetrathioborate complex was not achieved, an interesting organovanadium sulfide cluster $[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$, **2**, was generated from the pyrolysis of $[(CpV)_2(B_2H_6)_2]$, **1**, in *p*-xylene with sulfur powder (Scheme 1). Cluster **2** was obtained as an air-stable brown solid that was isolated by thin-layer chromatography (TLC) in 64% yield. **2** has been characterized spectroscopically as well as by single crystal X-ray diffraction analysis.

In the mass spectrum, the highest envelope was observed at *m*/*z* 425, consistent with $[(CpV)_2S_6]$. The ^{11}B NMR spectrum shows no boron resonances; however,

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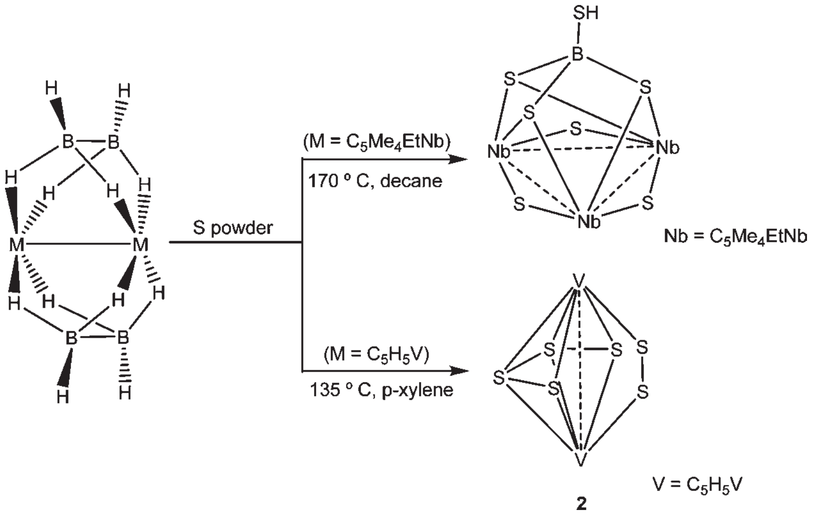
Scheme 1. Synthesis of Organovanadium Sulfide Cluster **2** and $[(\eta^5\text{-}C_5Me_4EtNb)_3BHS_7]$



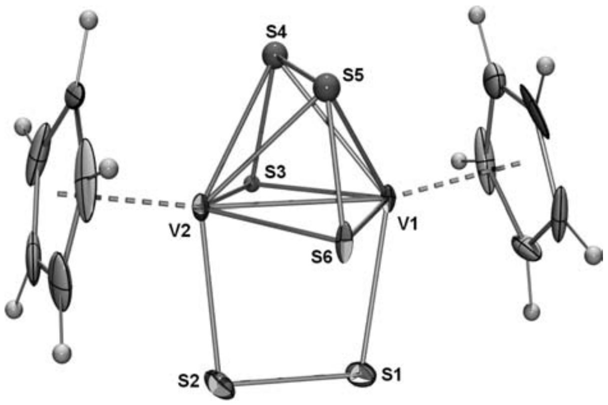


Figure 1. Molecular structure and labeling diagram for $[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$ **2.** Thermal ellipsoids are shown at the 30% probability level. Relevant bond lengths (Å) and angles (deg): V(1)−V(2), 2.665; V(1)−S(1), 2.335(3); V(2)−S(2), 2.332(3); V(1)−S(3), 2.342(5); V(1)−S(4), 2.391(4); V(1)−S(6), 2.416(4); S(1)−S(2), 2.037(2); S(3)−S(4), 1.904(7); S(4)−S(5), 2.175(4); S(5)−S(6), 2.098(6); S(5)−S(6)−V(1), 64.45(15); V(1)−S(6)−V(2), 67.50(9); V(2)−S(2)−S(1), 97.83(13); V(1)−S(3)−V(2), 68.98(11).

the ^{1}H NMR spectrum suggests a structure, if static, of higher symmetry. Consistent with this observation, the ^{13}C NMR of **2** also shows one kind of Cp signal. The infrared absorption bands of **2** observed at 789, 690, and 673 cm^{-1} may be attributed to different V−S bonding modes, whereas the absorption bands appear in the low-frequency region of the spectrum at 523 and 501 cm^{-1} have been assigned to S−S stretching modes.[31]

Single crystals suitable for X-ray diffraction analysis of **2** were obtained from a hexane/CH_2Cl_2 solution at −10 °C, thus allowing for the structural characterization of **2**. A solid-state structure determination of **2**, shown in Figure 1, shows that two vanadium ions are linked by a disulfide ligand which displays η^1 coordination to each metal atom in an end-on fashion.[32] The crystal structure solution and refinement shows 50% disorder each at the S3 and S6 atoms. In the absence of disorder for any other sulfur atom, the structure could only be interpreted as an equimolar co-crystal of $C_{10}H_{10}S_6V_2$ and $C_{10}H_{10}S_4V_2$. As there are no other meaningful disorder peaks near S4 and S5, assigning the structure as $C_{10}H_{10}S_6V_2$ alone is crystallographically incorrect.

Compound **2** is described as dimetallatetrahedron (V_2S_2) capped on each V_2S face with a (μ-η^2-S) ligand. The cage has C_{2v} symmetry with the vanadium atoms located in the apical positions and the four sulfur atoms in equatorial positions of the parent pentagonal bipyramidal polyhedron. The distance between the two sulfur atoms (S3 and S6) of 3.927 Å, positioned on the open face of the cluster, is much longer than the analogous S−S distance (3.117 Å), observed in metallathiaborane cluster $[(CpCo)_2S_2B_2H_2]$.[33] The V−V distance of 2.665 Å is at the appropriate range assigned to the V−V single bond.[18] The V−S−V angles are quite acute (V1−S3−V2 = 68.98 (11)°; V1−S6−V2 = 67.50 (9)°) and are indicative of a metal−metal interaction. The cyclopentadienyl ligands in **2** are symmetrically bonded to the vanadium atoms and are tilted from the mean plane of the four sulfur atoms such that the dihedral angle between them is 10.66°.

It has been observed that V−Cp(centroid) distances vary with the oxidation state of the metal: 1.87−1.92 Å for V(I), 1.91−1.92 Å for V(II), 1.94−1.96 Å for V(III), and 1.96−2.05 Å for V(IV).[34] The V−Cp(centroid) distances of 1.960 and 1.972 Å are indicative of a formal oxidation state of V(IV) for **2**. Further, the V−S distance provides an indication of sulfur to vanadium π donation. For example, V−S bond distance less than 2.35 Å reflect some π-bonding while longer V−S bonds indicate relatively innocent σ bonds.[15c] The V−S (μ-η^1-S_2) distance of 2.335 (3) Å in **2** indicates slightly V−S π bonding, similar to that observed for $[(C_5H_4Me)_2V_2S(PTD)(\mu\text{-}S_2Pt(PPh_3)_2)]$, (PTD = 4-Phenyl-l,2,4-triazoline-3,5-dione).[15d]

In the context of metal sulfide chemistry, the M_2S_6 core of **2** is unusual, and the occurrence of $M_2S_4(\mu\text{-}\eta^1\text{-}S_2)$ core is without precedent. Although only few dinuclear metal

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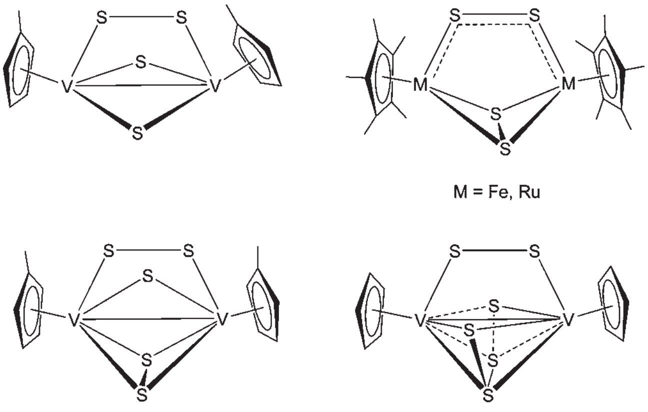
Chart 2. Bridging Disulfur Ligands Observed in Binuclear Complexes



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sulfides with (μ-η^1-S_2) ligand are reported,[17,18,22c,35,36] these have mostly M_2S_4 or M_2S_5 cores (Chart 2). The S−S (S1−S2) distance of 2.037(2) Å in **2** is the same as that observed in $[(i\text{-}PrC_5H_4)_2V_2S_4]$[22c] (2.027(3) Å), which is said to contain a *cis* supersulfide linkage between two vanadium atoms (Table 1). The dihedral angle about the S−S bond in **2** is 0°, as one finds in the superoxide bridge cobalt(III) complexes,[37] while the dihedral angle of close to 90° is normal for the disulfides.[38−40]

Synthesis and Characterization of $[(CpV)_2B_4H_{12-x}L_x]$ (3: L = SPh, x = 3; 4: L = SPh, x = 2; 5: L = SeBz, x = 1). Metallaborane and metallaheteroborane chemistry is extensive and has historically developed largely by the assimilation of one, two, or three atoms other than boron into the borane cluster.[26,41] The properties of metallaboranes are considerably different from those of pure boranes and carboranes, and it is not clear yet what factors will dominate the cluster growth or substitution reaction. The reaction of metallaboranes with $BHCl_2\cdot SMe_2$ resulted in the chlorination at cage B−H terminal bonds,[42] whereas $BH_3\cdot$thf leads to the cluster buildup reaction.[27,43] Thus, we explore the reactivity of diaryl disulfide and diselenide in the cluster building process to access products not found with chalcogen powders (S, Se). Klumpp and co-workers have first reported the reactivity of dialkyl and diaryl disulfides with metal carbonyl fragments in which they have observed that RSSR ligands (R = alkyl or aryl) act as a source of both "S" and "SR",[44] and the product distribution varies greatly, depending on the nature of the R group.

With this in mind, the reaction of the vanadaborane complex $[(CpV)_2(B_2H_6)_2]$ **1**, with diphenyl disulfide and dibenzyl diselenide have been investigated. The objective of generating metallaheteroborane clusters was not achieved; however, new cage substituted products were isolated. As shown in Scheme 2, thermolysis of $[(CpV)_2(B_2H_6)_2]$ **1** with *bis*-chalcogenide ligands (Ph_2S_2 or Bz_2Se_2) in *p*-xylene yielded B−L (L = SPh or SeBz) inserted metallaborane products, **3**−**5** (**3**: $[(CpV)_2B_4H_9(PhS)_3]$, **4**: $[(CpV)_2B_4H_{10}(PhS)_2]$, **5**: $[(CpV)_2B_4H_{11}(BzSe)]$). In the case of dibenzyl diselenide only the mono substituted product, **5** was isolated; however, in the case of diphenyl disulfide both di- and trisubstituted vanadaboranes, **3**, **4** were isolated. The reactions were monitored by ^{11}B NMR spectroscopy, which revealed formation of new boron containing compounds, as indicated by the presence of resonance in the ^{11}B NMR spectrum at δ = 15 to −5 ppm. Compound **3**−**5** have been characterized spectroscopically (^{1}H, ^{13}C, ^{11}B NMR) as well as by single crystal X-ray diffraction analysis.

Compounds **3** and **4** have been isolated following thin layer chromatography (TLC) in yields of 19% and 31%, respectively. The mass spectrometry measurement of **3** gives a molecular ion corresponding to $C_{28}H_{34}B_4V_2S_3$. The $^{11}B\{^1H\}$ NMR spectrum shows one type of BH and one type of B−SPh environment in a ratio of 1:3. The resonance at δ = 7.9 ppm showed no coupling in ^{11}B NMR which confirms the presence of three B−SPh environments and it is an accidental overlap of three ^{11}B resonances. The peak at δ = −0.46 arises from the B−H group, and it showed the usual coupling in the ^{11}B spectrum. Furthermore, the $^1H\{^{11}B\}$ NMR spectrum shows one type of Cp protons and two types of V−H−B protons at δ = −8.0 and −8.9 ppm in the ratio of 6:2. The ^{13}C NMR spectrum also reveals the presence of one Cp resonance. The IR spectrum of **3** shows a band at 2426 cm^{-1} in a region characteristic of the B−H stretching frequency.

The molecular structure of **3**, determined by X-ray diffraction study, is shown in Figure 2. Its geometry is similar to that of the parent molecule $[(CpV)_2(B_2H_6)_2]$ **1**, and it is described as a metallaborane built from two edge-fused V_2B_2 tetrahedra. The V−V, avg. B−B and avg. V−B bond distances of 2.831, 1.74, and 2.317 Å in **3** are comparable with that of **1**.

The FAB mass analysis of **4** gives a molecular ion peak corresponding to $(CpV)_2B_4H_{10}(PhS)_2$. Both ^{11}B NMR and ^{1}H NMR spectra of **4** indicate a highly symmetrical molecule. The ^{11}B NMR rationalizes the presence of two boron resonances in the ratio of 2:2 where the resonance at δ = 10.1 ppm showed no coupling in ^{11}B NMR confirms the B−SPh environment. Furthermore, ^{1}H and ^{13}C NMR spectra imply one kind of Cp ligand. Similarly, the $^1H\{^{11}B\}$ NMR spectrum also reveals one type of B−H proton and the presence of two kinds of

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Table 1. Selected Structural Parameters of **2** and Related Organodimetallic Sulfide Complexes

compound	*d*[M−M] [Å]	avg. *d*[M−S][a] [Å]	*d*[S−S][b] [Å]	avg. [M−S−M][c] [deg]	ref.
$[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$ **2**	2.665	2.333	2.037	68.23	this work
$[(i\text{-}PrC_5H_4V)_2S_2(\mu\text{-}\eta^1\text{-}S_2)]$	2.610	2.274	2.027		22c
$[(C_5H_4MeV)_2S_3(\mu\text{-}\eta^1\text{-}S_2)]$	2.658	2.315	2.023	69.4	18
$[(C_5Me_4EtRu)_2S_2(\mu\text{-}\eta^1\text{-}S_2)]$	3.749	2.20	2.020	104.1	17
$[(CpFe)_2S_2(\mu\text{-}\eta^1\text{-}S_2)]$	3.494	2.105	1.999	101.1	35

[a] The average distance between metal and (μ-η^1-S_2) ligand. [b] Distance between (μ-η^1-S_2) atoms. [c] The average angle of metal−(μ-η^2-S)−metal.

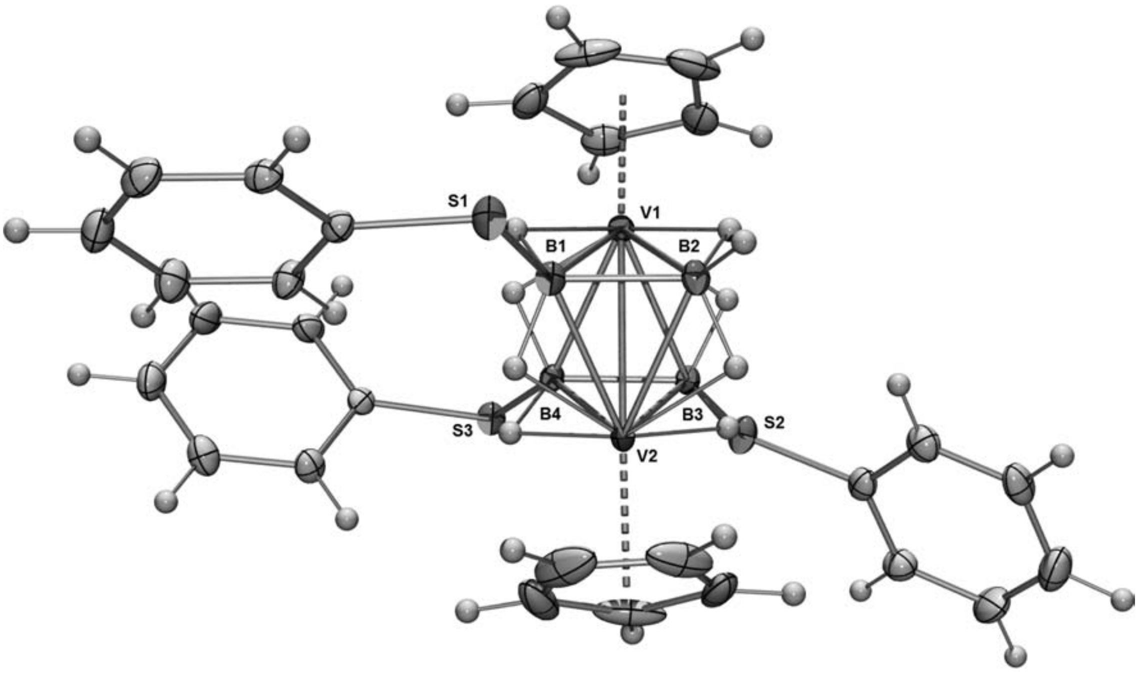
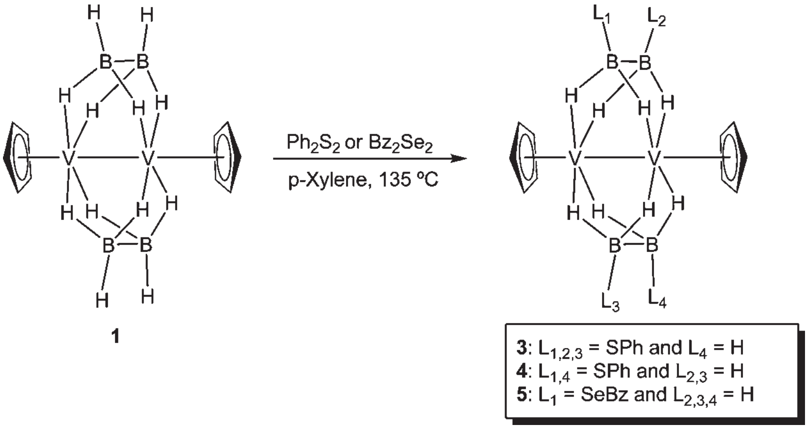


Figure 2. Molecular structure and labeling diagram for $[(CpV)_2B_4H_9(PhS)_3]$ **3**. Thermal ellipsoids are shown at the 30% probability level. Relevant bond lengths (Å) and angles (deg): V(1)−V(2), 2.8318(5); V(1)−B(1), 2.322(3); V(2)−B(2), 2.327(3); B(1)−B(2), 1.746(4); B(3)−B(4), 1.748(3); B(1)−S(1), 1.876(3); B(3)−S(2), 1.865(3); B(4)−S(3), 1.884(2); S(1)−B(1)−B(2), 111.56(16); V(1)−B(1)−V(2), 75.11(8); B(4)−V(1)−B(1), 88.12(9).

Scheme 2. Synthesis of B-Chalcogenide Vanadaborane Derivatives **3**−**5**



V−H−B protons each at $\delta = -8.4$ and -9.5 ppm of intensity ratio 4:4.

Single crystals suitable for X-ray diffraction analysis of **4** were obtained from a mixture of hexane/CH_2Cl_2 solution at −4 °C, thus allowing the structural characterization of $[(CpV)_2B_4H_{10}(PhS)_2]$ and confirming the structural inferences made on the basis of spectroscopic results. The molecular structure of **4** in the solid state is shown in Figure 3, where this compound is seen to be a cluster analogue of **1** and $[(CpNb)_2(B_2H_6)_2]$.[29] The bond angle of the B−S−Ph group (105.7°) in **4** suggested that it is closed to the expected value for the sulfur atom in the sp^3 hybridization.[45]

The composition of **5** is recognized from the mass spectral analysis together with multinuclear NMR spectroscopy. The mass spectrum of the compound showed a

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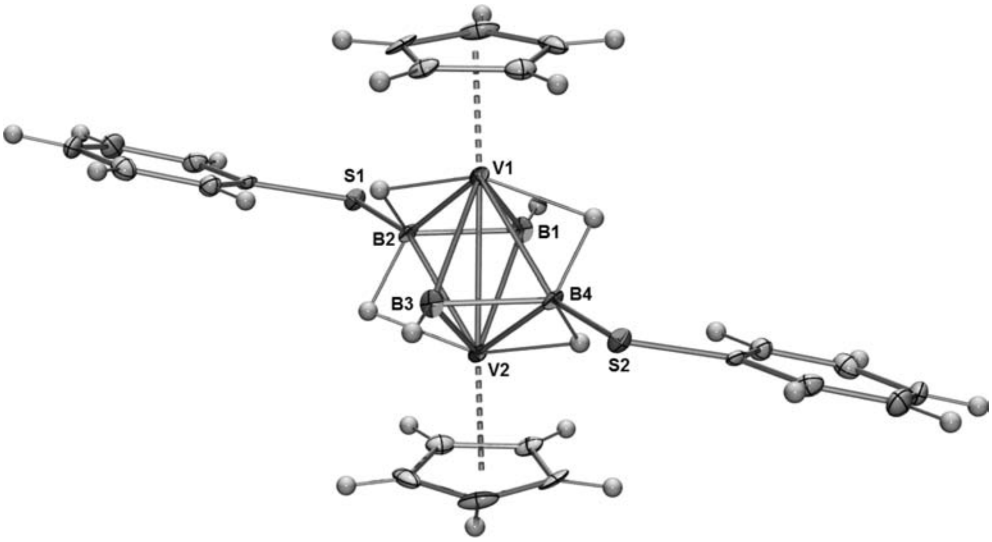

Figure 3. Molecular structure and labeling diagram for $[(CpV)_2B_4H_{10}(PhS)_2]$ **4**. Thermal ellipsoids are shown at the 30% probability level. Relevant bond lengths (Å) and angles (deg): V(1)−V(2), 2.827(2); V(1)−B(1), 2.314(9); V(1)−B(2), 2.319(9); V(1)−B(3), 2.325(9); V(2)−B(2), 2.322(8); B(1)−B(2), 1.781(12); B(2)−S(1), 1.871(8); B(2)−V(1)−B(1), 45.2(3); B(3)−V(1)−B(1), 104.9(3); B(2)−V(1)−B(4), 105.0(2); B(1)−V(1)−B(4), 88.0(3).

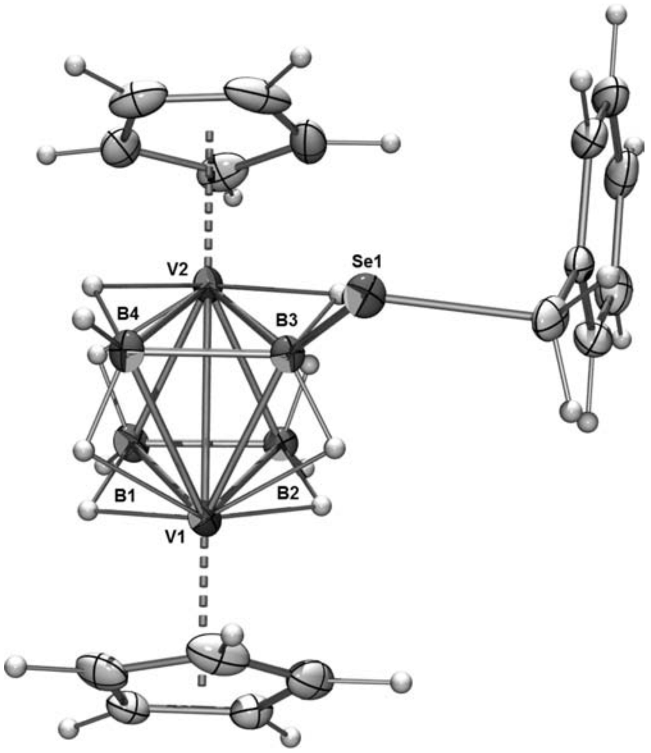

Figure 4. Molecular structure and labeling diagram for $[(CpV)_2B_4H_{11}(BzSe)]$ **5**. Thermal ellipsoids are shown at the 30% probability level. Relevant bond lengths (Å) and angles (deg): V(1)−V(2), 2.8054(9); V(1)−B(1), 2.300(4); V(1)−B(2), 2.314(4); V(2)−B(2), 2.304(5); V(2)−B(1), 2.308(5); B(1)−B(2), 1.768(6); B(3)−B(4), 1.744(6); B(3)−Se(1), 2.011(4); B(2)−B(1)−V(1), 67.90(19); V(1)−B(1)−V(2), 75.01(13); V(1)−B(3)−B(4), 68.3(2); Se(1)−B(3)−V(2), 142.3(2).

single parent ion corresponding to $C_{17}H_{28}B_4V_2Se$ which is consistent with the formula containing four B, two V, and one Se atoms. The ^{11}B NMR spectrum of **5** exhibits three signals at $\delta = 6.7$, 2.9, and −1.2 ppm with 1:2:1 ratio. The resonance in this spectrum at $\delta = 6.7$ ppm is ascribed to the B−SeBz nucleus as it remained a singlet in the fully coupled ^{11}B spectrum, whereas the other peaks became doublets. The $^1H\{^{11}B\}$ spectrum suggests the presence of two kind of terminal H atoms and two kinds of bridging H atoms, at $\delta = -8.4$ and −9.8 ppm.

The molecular structures of **5** shown in Figure 4 are consistent with the analysis of the observed spectroscopic data and reveal core geometries that are the same as those observed for **1**. The V−B bond lengths of **5** range from 2.30 Å to 2.31 Å, and the B−B distances range from 1.74 Å to 1.76 Å are similar to those observed in **3** and **4**. The Se−B distance (2.011(4) Å) in **5** is somewhat shorter than those (2.016(15) and 2.023(16) Å) in the salt $[NEt_4]_2[Se_3B_{11}H_9]$, a disubstituted derivative of [*closo*-$B_{11}H_{11}]^{2-}$ in which an Se_3 chain bridges two boron atoms.[46] The bond angle of the B−Se−C group (101.1°) in **5** suggests that the selenium atom is sp^3 hybridized.

The existence of compounds **3**−**5** permits a structural comparison with **1**. In Table 2 we have summarized the comparison of the structural parameters and ^{11}B NMR of **3**−**5** with **1**. The V1−V2 bond distance in compounds **3**−**5** is significantly longer than the parent molecule $[(CpV)_2(B_2H_6)_2]$ **1**. The avg. V−B and B−B distances are also noticeably longer in **3**−**5**; in contrast the dihedral angles of the hydrogen bridged butterfly face are shorter than in **1**. The average distance between vanadium and boron atoms which are attached to a chalcogenide ligand is less than those of boron which attached to hydrogen atoms. Difference in the observed structural parameters and ^{11}B NMR chemical shift correlation of **3**, **4**, and **5** with **1** may be due to the perturbation of the electronic environment of the boron atoms by the ligand.

Conclusion

Although a rich chemistry of the cyclopentadienylvanadium sulfides are well documented, the core geometry of **2** is unprecedented. One of the interesting features of **2** is the plane of the four sulfur atoms, perpendicular to the metal−metal bond and parallel to the two Cp rings, in which the $[V_2S_4]$ atoms define a bicapped tetrahedron framework, with

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[46] Freiser, G. D.; Little, J. L.; Huffmann, J. C.; Todd, L. J. *Inorg. Chem.* **1979**, *18*, 755.

Table 2. Comparison of Selected Structural Parameters of Compounds **3**−**5** with **1**

complexes	*d*[V1−V2] [Å]	avg. *d*[V−B][a] [Å]	avg. *d*[V−B][b] [Å]	avg. *d*[B−B] [Å]	dihedral angle[c] [deg]	^{11}B NMR ppm
$[(CpV)_2(B_2H_6)_2]$ **1**	2.787		2.296	1.73	123.0	1.7
$[(CpV)_2B_4H_9(PhS)_3]$ **3**	2.831	2.310	2.324	1.74	122.4	7.9, −0.4
$[(CpV)_2B_4H_{10}(PhS)_2]$ **4**	2.827	2.321	2.321	1.78	122.1	10.1, −0.3
$[(CpV)_2B_4H_{11}(BzSe)]$ **5**	2.805	2.300	2.309	1.75	122.3	6.7, 2.9, −1.2

[a] The average distance between vanadium and boron atoms which are attached to a chalcogenide ligand. [b] The average distance between vanadium and boron atoms which are attached to a hydrogen atom. [c] Dihedral angles of the hydrogen bridged butterfly face.

Table 3. Crystallographic Data and Structure Refinement Information for **2**−**5**

	2	**3**	**4**	**5**
empirical formula	$C_{10}H_{10}S_5V_2$[a]	$C_{28}H_{34}B_4S_3V_2$	$C_{22}H_{26}B_4S_2V_2$	$C_{17}H_{28}B_4SeV_2$
formula weight	392.36 [b]	611.85	499.69	456.47
crystal system	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P2_1/c$	*Pbca*	$P\bar{1}$
a (Å)	13.885(3)	12.4162(4)	9.8140(18)	10.5962(4)
b (Å)	7.0801(14)	16.4868(5)	11.7167(15)	13.0475(6)
c (Å)	13.914(3)	14.5421(4)	19.958(3)	15.7719(7)
α (deg)	90	90	90.00	103.698(2)
β (deg)	91.75(2)	102.8850(10)	90.00	100.197(2)
γ (deg)	90	90	90.00	101.929(2)
V (Å^3)	1367.2(5)	2901.86(15)	2294.9(6)	2013.33(15)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.906	1.400	1.435	1.506
F (000)	784	1264	1008	920
μ (mm^{-1})	2.101	0.877	1.003	2.732
crystal size (mm)	0.42 × 0.22 × 0.20	0.42 × 0.26 × 0.09	0.22 × 0.18 × 0.06	0.38 × 0.28 × 0.08
θ range (deg)	1.46- 28.17	1.68−28.42	2.04−26.85	1.66-31.27
no. of total refins collected	9108	21493	5682	31705
no. of unique refins [$I > 2\sigma(I)$]	3046	7142	1740	11586
max and min transmission	0.722 and 0.523	0.9252 and 0.7095	0.9422 and 0.8094	0.8111 and 0.4233
data/restraints/parameters	3046/0/155	7142/0/370	1740/0/140	11586/1/556
goodness-of-fit on F^2	1.154	1.025	1.025	1.024
final *R* indices [$I > 2\theta(I)$]	R1 = 0.0684	R1 = 0.0412	R1 = 0.0597	R1 = 0.0537
	wR2 = 0.1523	wR2 = 0.1318	wR2 = 0.1397	wR2 = 0.1439
R indices (all data)	R1 = 0.0860	R1 = 0.0541	R1 = 0.1178	R1 = 0.0935
	wR2 = 0.1661	wR2 = 0.1451	wR2 = 0.1966	wR2 = 0.1682
largest difference in peak and hole (e/Å^3)	1.535and −1.351	0.832 and −0.849	0.660 and −0.955	2.199 and −0.881

[a] Sum of the chemical formula of $0.5(C_{10}H_{10}S_6V_2)$ and $0.5(C_{10}H_{10}S_4V_2)$. [b] The average formula weight of **2** and $C_{10}H_{10}S_4V_2$.

one μ-η^1-S_2 ligand bridged the two (CpV) moieties. The μ-S_2 ligand in **2** is of particular interest because it represents a reactive cluster-bound functional group which may be employed for organic synthesis, for the assembly of unusual mixed-metal clusters, or as hydrogenation catalysts. Furthermore, the exocluster substitution at B−H in vanadaborane cluster, $[(CpV)_2(B_2H_6)_2]$ **1** was achieved by the pyrolysis with *bis*-chalcogenide ligands (Ph_2S_2 or Bz_2Se_2), results in the formation of the substituted vanadahexaboranes **3**−**5**.

Experimental Section

General Procedures and Instrumentation. All the operations were conducted under an Ar/N_2 atmosphere using standard Schlenk techniques or glovebox. Solvents were distilled prior to use under Argon. $[(Cp)_2VCl_2]$, $[BH_3\cdot thf]$, $[LiBH_4\cdot thf]$, sulfur, and selenium powder (Aldrich) were used as received. $[(CpV)_2(B_2H_6)_2]$,[29] Ph_2S_2,[47] and Bz_2Se_2[48] were prepared as described in literature. The external reference for the ^{11}B NMR, $[Bu_4N(B_3H_8)]$, was synthesized with the literature method.[49] 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, [D$_6$]benzene, 7.16), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in [D$_6$]benzene (δ_B, ppm, −30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet 6700 FT spectrometer. Mass spectra were obtained on a Jeol SX 102/Da-600 mass spectrometer with argon/xenon (6kv, 10 mÅ) as FAB gas.

Synthesis of $[(CpV)_2S_4(\mu\text{-}\eta^1\text{-}S_2)]$ (2). To a 100 mL Schlenk tube containing 0.08 g (0.28 mmol) of $[(CpV)_2(B_2H_6)_2]$, **1** in 12 mL of *p*-xylene was added slowly to 3 equiv of sulfur powder (0.026 g, 0.84 mmol). The reaction mixture was thermolyzed at 135 °C for 16 h and cooled to room temperature. Volatiles were removed in vacuo, and the residue was extracted into toluene and filtered through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (80:20 v/v) mixture yielded brown **2** (0.075 g, 64%). ^{1}H NMR ([D$_6$]benzene, 22 °C, 400 MHz): δ 6.13 (s, 10H; Cp). ^{13}C NMR ([D$_6$]benzene, 22 °C, 100 MHz): δ 104.2 (s; C_5H_5). IR (hexane) ν/cm^{-1}: 789vs, 690s, 673s, 523w, and 501w. MS (FAB) P$^+$(max): *m*/*z*(%): 425 (isotopic pattern for two V and six S atoms). Elemental analysis (%) calcd for $^{12}C_{10}{}^1H_{10}{}^{50}V_2{}^{32}S_5$: C, 30.60; H, 2.56. Found: C, 30.03; H, 2.41.

General Synthesis of 3−5. In a typical reaction $[(CpV)_2(B_2H_6)_2]$, **1** (0.06 g, 0.21 mmol) in *p*-xylene (10 mL) was stirred with 4 equiv of Ph_2S_2 (0.18 g, 0.84 mmol) for 16 h at 135 °C. Volatiles were removed in vacuo, and the residue was extracted in hexane and filtered through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (80:20 v/v) mixture yielded light green $[(CpV)_2B_4H_9(PhS)_3]$,

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3 (0.03 g, 19%) and dark green [$(CpV)_2B_4H_{10}(PhS)_2$], **4** (0.04 g, 31%). Under the same reaction conditions green [$(CpV)_2B_4H_{11}(BzSe)$], **5** (0.02 g, 21%) was isolated from the reaction of **1** and Bz_2Se_2.

3. ^{11}B NMR ([D_6]benzene, 22 °C, 128 MHz): δ 7.9 (s, br, 3B), −0.4 (d, 1B, BH). ^{1}H NMR ([D_6]benzene, 22 °C, 400 MHz): δ 5.96 (s, 10H; Cp), 3.1 (partially collapsed quartet (pcq), 1BH_t), −8.09 (br, 6 V−H−B), −8.93 (br, 2 V−H−B). ^{13}C NMR ([D_6]benzene, 22 °C, 100 MHz): δ 100.8 (s; C_5H_5). IR (hexane) ν/cm^{-1}: 2426w (BH_t). MS (FAB) P^+(max): *m*/*z*(%): 612 (isotopic pattern for 2 V, 4B and 3S atoms).

4. ^{11}B NMR ([D_6]benzene, 22 °C, 128 MHz): δ 10.1 (s, br, 2B), −0.3 (d, 2B; BH). ^{1}H NMR ([D_6]benzene, 22 °C, 400 MHz): δ 5.94 (s, 10H; Cp), 2.89 (pcq, 2BH_t), −8.45 (br, 4 V−H−B), −9.54 (br, 4 V−H−B). ^{13}C NMR ([D_6]benzene, 22 °C, 100 MHz): δ 100.1 (s; C_5H_5). IR (hexane) ν/cm^{-1}: 2401w (BH_t). MS (FAB) P^+(max): *m*/*z*(%): 503 (isotopic pattern for 2 V, 4B and 2S atoms). Elemental analysis (%) calcd for $^{12}C_{22}{}^{1}H_{26}{}^{50}V_2{}^{32}S_2{}^{11}B_4$: C, 52.87; H, 5.24. Found: C, 50.96; H, 5.07.

5. ^{11}B NMR ([D_6]benzene, 22 °C, 128 MHz): δ 6.7 (s, br, 1B), 2.9 (d, 2B; BH), −1.2 (d, 1B; BH). ^{1}H NMR ([D_6]benzene, 22 °C, 400 MHz): δ 5.48 (s, 10H; Cp), 3.5 (pcq, 1BH_t), 2.26 (pcq, 2BH_t), −8.44 (br, 2 V−H−B), −9.83 (br, 6 V−H−B). ^{13}C NMR ([D_6]benzene, 22 °C, 100 MHz): δ 129.0, 128.5, 127.5, 127.1 (C_6H_5), 101.4 (s; C_5H_5), 31.9 (s, PhCH_2Se). IR (hexane) ν/cm^{-1}: 2456w (BH_t). MS (FAB) P^+(max): *m*/*z*(%): 456 (isotopic pattern for 2 V, 4B and 1Se atoms). Elemental analysis (%) calcd for $^{12}C_{17}{}^{1}H_{28}{}^{50}V_2{}^{78}Se{}^{11}B_4$: C, 44.72; H, 6.18. Found: C, 46.07; H, 6.30.

X-ray Structure Determination. Crystallographic information for the compounds is given in Table 3. The crystal data for **2**−**5** were collected and integrated using a Bruker AXS kappa apex2 CCD diffractometer, with graphite monochromated Mo−Kα (λ = 0.71073 Å) radiation at 173 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92[50] and refined using SHELXL-97 (Sheldrick, G.M., University of Göttingen).[51,52]

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Supporting Information Available: The supplementary crystallographic data and X-ray crystallographic files for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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