

## Synthesis and structural characterization of an open cage dithiatungstaborane [(CpW)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] cluster

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Reaction of Cp<sup>#</sup>MCl<sub>4</sub>, (**1** or **2**) [(**1**): M = Mo, Cp<sup>#</sup> = Cp\* (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) and (**2**): M = W, Cp<sup>#</sup> = Cp (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] with excess of [LiBH<sub>4</sub>.thf] followed by thermolysis with excess of [HS(CH<sub>2</sub>)<sub>n</sub>SH] (n = 2 or 3), leads to the formation of [(Cp\*Mo)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] (**3**) or [(CpW)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] (**4**) respectively. Corresponding to (**3**) and (**4**), the compounds [(M)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] (M = CpW, (**5**) or Cp\*Mo, (**6**)) are isolated as major product in both the cases. These new compounds have been characterized in solution by mass, <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C NMR spectroscopy. The structural types have been unequivocally established by X-ray crystallographic analysis of compounds (**4**).

**Keywords:** Coordination Chemistry, Metallaboranes, Open cage compounds, Chalcogens, Metallaheteroborane clusters, Tungsten, Boron

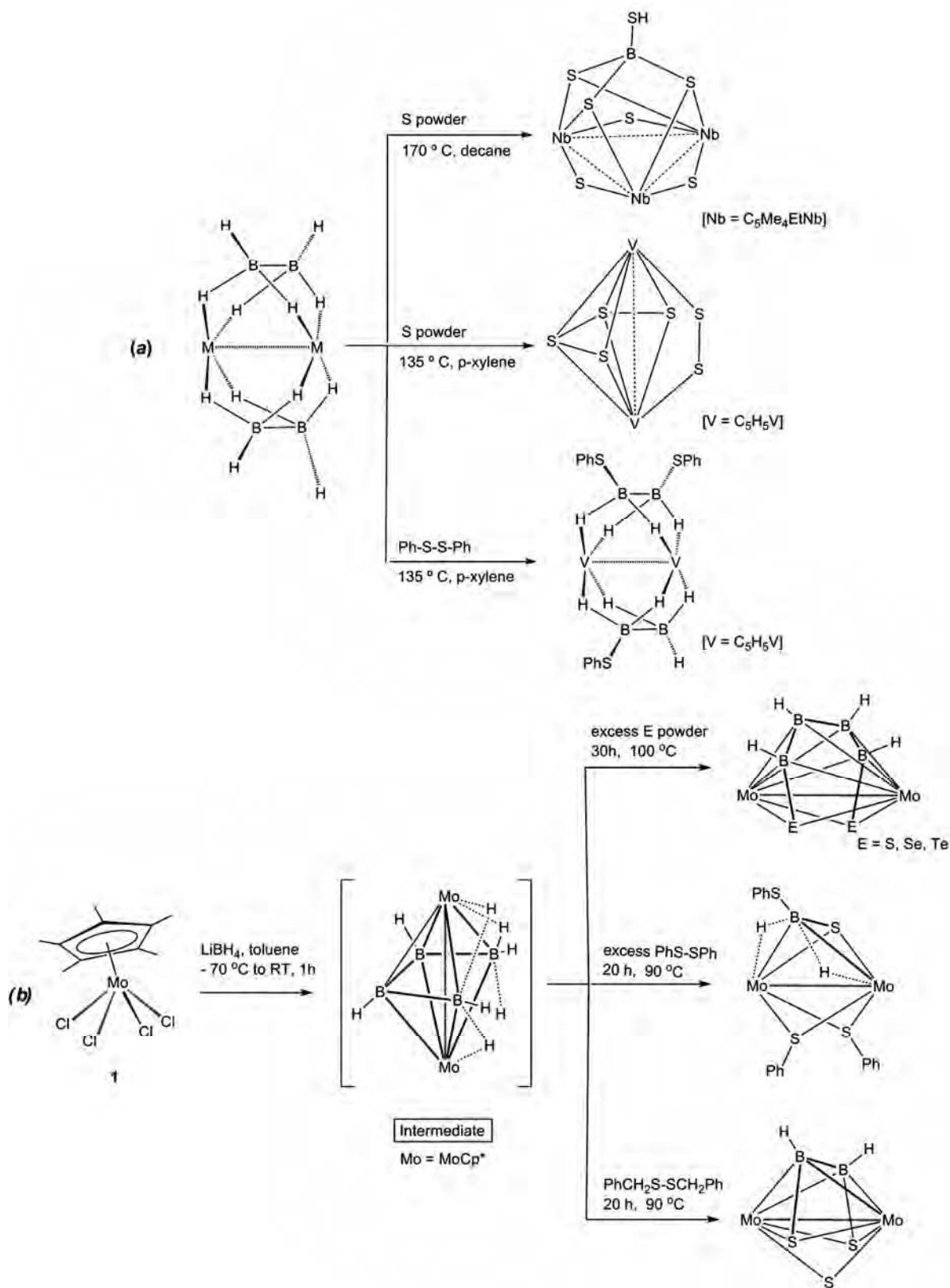
An area of continuing importance in polyhedral metallaborane chemistry is the development of new efficient methods in which atom-insertion reactions leading to expanded-cage clusters may be accomplished. Although the structural variety of polyhedral metallaborane chemistry is, in theory, also accessible to any combinations of main-group elements that have the same numbers of valence electrons, this chemistry is dominated typically by carboranes and metallacarboranes.<sup>1-6</sup>

Metallaheteroborane compounds containing group 16 elements as a cluster constituent have mostly been generated from the reaction of metal centres with pre-formed polyhedral heteroborane substrates<sup>7-18</sup>. Although there are several reports of the synthesis of these compounds available in the literature, it was found that the number of metallaheteroboranes prepared using metallaboranes remains rather limited<sup>19-23</sup>. As part of our ongoing studies on metallaheteroboranes, our research group recently described the synthesis and reactivity of a series of dichalcometallaborane clusters of group 5-9 metals,<sup>24-28</sup> obtained from the pyrolysis of several chalcogen sources and reactive metallaborane intermediates (Scheme 1). As dimetallaheteroboranes are rare, and structurally characterized examples are even more so, we have begun to investigate the use of new chalcogen sources which might result in the generation of new types of metallaheteroborane

cluster systems. The reaction can involve ligand exchange, ligand addition, or metal(s) incorporation either into the cage or as *exo*-polyhedral moieties. In this paper, we present a new set of chalcogen sources [HS(CH<sub>2</sub>)<sub>n</sub>SH], (n = 2, 3) which afforded dimetallathiorboranes (**3**) and (**4**) in moderate to good yields.

### Materials and Methods

All the experiments were conducted under an Ar/N<sub>2</sub> atmosphere using standard Schlenk techniques. The solvents were distilled prior to use under Argon. CpH, Cp\*H, W(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, BuLi, [BH<sub>3</sub>.thf], [LiBH<sub>4</sub>.thf], [HS(CH<sub>2</sub>)<sub>n</sub>SH, n = 2, 3] (Aldrich) were used as received. MeI was purchased from Aldrich and freshly distilled prior to use. Compounds (**1**) and (**2**) were prepared with some modification<sup>29</sup> of the work of Green *et al.*<sup>30</sup> The external reference, [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)], for the <sup>11</sup>B NMR was synthesized by literature method<sup>31</sup>. Thin layer chromatography (TLC) was carried out on 250 mm dia. aluminum supported silica gel TLC plates (Merck). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl<sub>3</sub>, 7.26), while a sealed tube containing [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)] in C<sub>6</sub>D<sub>6</sub> (δ<sub>B</sub>, ppm, -30.07) was used as an external reference for the <sup>11</sup>B NMR. Infrared spectra were obtained on a Nicolet 6700 FT-IR spectrometer.


 Reactivity of different chalcogen sources with (a)  $[(\text{M})_2(\text{B}_2\text{H}_6)_2]$  ( $\text{M} = \text{CpV}$  and  $\text{C}_5\text{Me}_4\text{EtNb}$ ); (b)  $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_8]$ 

Scheme 1

**General method for the synthesis of 3 and 4, [(Cp<sup>#</sup>M)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] [(3): M = Mo, Cp<sup>#</sup> = Cp\*; (4): M = W, Cp<sup>#</sup> = Cp]**

To [Cp<sup>#</sup>MoCl<sub>4</sub>], (1) (0.5 g, 1.34 mmol) in 20 mL of toluene, was added 6-fold excess of [LiBH<sub>4</sub>.thf] (4.03 mL, 8.05 mmol) at -40 °C. The mixture was stirred at room temperature for one hour. After removal of toluene the residue was extracted with hexane. The extract was filtered through a frit using Celite. The yellowish green hexane extract was dried and taken in 25 mL of toluene. The resulting solution was heated at 100 °C with a 3-fold excess of [HS(CH<sub>2</sub>)<sub>2</sub>SH] (0.36 mL, 4.03 mmol) or HS(CH<sub>2</sub>)<sub>3</sub>SH (0.4 mL, 4.03 mmol for Mo) for 18 h. The solvent was evaporated in vacuo and the residue was extracted with hexane. The hexane solution was passed through Celite mixed with a small amount of silica gel. After removal of solvent from the filtrate, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with hexane yielded the orange [(Cp<sup>#</sup>Mo)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] (3) (0.12 g, 15%).

Under the same reaction conditions, [CpWCl<sub>4</sub>] (2) (0.5 g, 1.27 mmol) and [HS(CH<sub>2</sub>)<sub>2</sub>SH] (0.34 mL, 3.84 mmol) or [HS(CH<sub>2</sub>)<sub>3</sub>SH] (0.38 mL, 3.84 mmol) yielded respectively the orange [(CpW)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] (4) (0.04 g, 6%), and the orange [(CpW)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] (5) (0.15 g, 21%). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 22 °C, 128 MHz): δ = 74.9 (d, J<sub>B-H</sub> = 158 Hz, 2B), -10.6 (d, J<sub>B-H</sub> = 168 Hz, 2B); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C, 400 MHz): δ = 8.42 [partially collapsed quartet (*pcq*), 2BH<sub>i</sub>], 5.69 (s, 10H, Cp), 4.31 (*pcq*, 2BH<sub>i</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22 °C, 100 MHz): δ = 93.2 (s, C<sub>5</sub>H<sub>5</sub>); IR (hexane, cm<sup>-1</sup>): 2510w (B-H<sub>i</sub>).

Note that compounds [*nido*-(Cp<sup>#</sup>Mo)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>S<sub>2</sub>] (3) and [*nido*-(Cp<sup>#</sup>Mo)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] have been isolated and characterized by comparison with their spectroscopic data reported earlier<sup>24,32</sup>. The [*nido*-(CpW)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] has been isolated and characterized by comparison with the spectroscopic data reported for its Cp<sup>#</sup> analogue<sup>33</sup>.

#### X-ray data collection and refinement

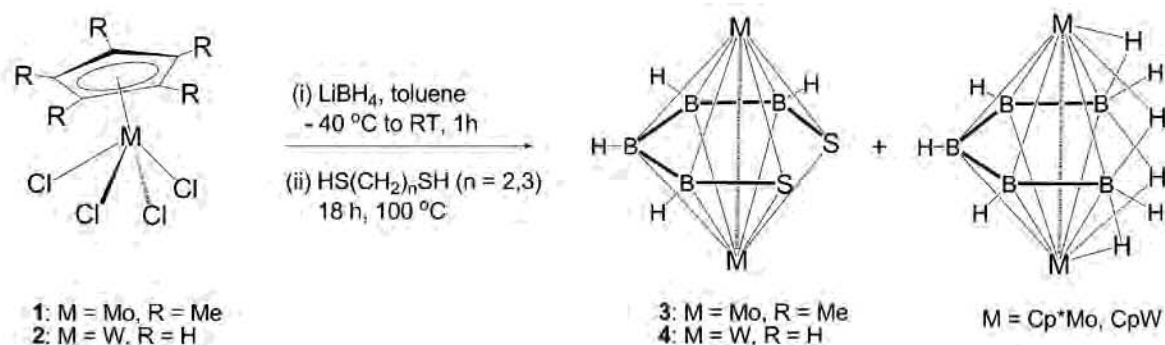
Crystallographic information for the compound (4) is given in Table 1. Suitable crystals of (4) were obtained from hexane/CH<sub>2</sub>Cl<sub>2</sub> (9:1) mixture at -4 °C. The crystal data were collected and integrated using a Bruker Axs Kappa Apex2 CCD diffractometer system equipped with graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) at 173 K. The structures were solved by heavy atom methods using SHELXS-97<sup>34</sup> and refined using SHELXL-97<sup>35</sup>.

## Results and Discussion

As shown in Scheme 2, reaction of (1) or (2) with a six-fold excess of [LiBH<sub>4</sub>.thf], followed by thermolysis with 1,2-ethane or 1,3-propane dithiol in toluene at 100 °C yielded (3) or (4) along with [(Cp<sup>#</sup>M)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] (M = Mo: Cp<sup>#</sup> = Cp\*; M = W; Cp<sup>#</sup> = Cp). All the reactions were monitored by <sup>11</sup>B NMR spectroscopy, which revealed formation of the new boron containing compounds, as indicated by the presence of two resonances in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum at δ = -10 to 80 ppm region. These compounds can be separated by thin layer chromatography (TLC), which allowed spectroscopic and structural characterization of pure materials. These reactions utilized [HS(CH<sub>2</sub>)<sub>n</sub>SH] (n = 2 or 3) ligands as a chalcogen source and the presence of the same number of boron framework atoms in (3) or (4) proved that the dichalcogen ligands stabilized the metallaborane intermediates. Further, as shown in Scheme 1 and 2, the difference in reactivity pattern of different chalcogen sources with metallaboranes is also reflected in the observed products distribution. Compound (3) has also been isolated earlier from the pyrolysis of S powder and an *in situ* generated intermediate [(Cp<sup>#</sup>Mo)<sub>2</sub>B<sub>4</sub>H<sub>8</sub>], produced from the reaction of (1) and [LiBH<sub>4</sub>.thf] at low temperature. However, several attempts to directly isolate the W

Table 1—Crystallographic data and refinement parameters for compound (4)

Formula	C <sub>10</sub> H <sub>10</sub> B <sub>4</sub> S <sub>2</sub> W <sub>2</sub>
Formula weight	605.24
Color	Orange
Crystal system	Monoclinic
Crystal size	0.25 × 0.20 × 0.09
Space group	C2/c
a (Å)	10.1398(15)
b (Å)	11.9577(14)
c (Å)	12.469(2)
α (°)	90.00
β (°)	110.416(4)
γ (°)	90.00
V (Å <sup>3</sup> )	1416.9(4)
Z	4
D <sub>calc</sub> (mg/m <sup>3</sup> )	2.837
F (000)	1080
μ (mm <sup>-1</sup> )	16.490
θ Range (°)	2.74 – 28.61
Goodness-of-fit	1.663
R indices [ <i>I</i> > 2σ( <i>I</i> )]	R1 = 0.0831, wR2 = 0.2335
R indices (all data)	R1 = 0.0950, wR2 = 0.2396



## Synthesis of dithiatungstaborane (4)

## Scheme 2

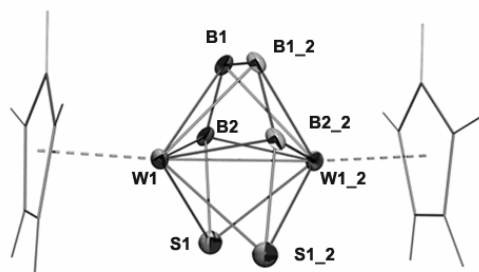


Fig. 1 — Molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5\text{W})_2\text{B}_4\text{H}_4\text{S}_2]$  (**4**). [The thermal ellipsoids correspond to 30 % probability].

analogue failed, partly because of the instability of this compound under the above conditions. Therefore, an attempt was made to isolate the W analogue of (**3**) (Cp analogue) from  $[\text{CpWCl}_4]$ , which yielded (**4**), albeit in low yield.

*nido*- $[(\text{CpW})_2\text{B}_4\text{H}_4\text{S}_2]$  (**4**)

Compound (**4**) has been isolated in 6 % yield from the reaction mixture and characterized in comparison with its spectroscopic data with other similar complexes  $[\text{Cp}^*\text{MB}_4\text{H}_4\text{E}_2]$  (M = Mo, E = S, Se and Te; M = W: E = Se)<sup>24</sup>. The  $^{11}\text{B}$  chemical shifts of (**4**) which appeared at  $\delta = 74.9$  and  $-10.6$  ppm in the ratio 1:1, are in good agreement with those of  $[(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_4\text{Se}_2]$ <sup>24</sup>. The sharp  $^{11}\text{B}$  NMR resonance at  $\delta = -10.6$  ppm has been assigned to the boron atoms, which are attached to sulfur atoms. Consistent with this observation,  $^1\text{H}$  NMR shows the presence of four B-H terminal protons (1:1) and one kind of Cp ligand at  $\delta = 5.69$  ppm.

The single crystal X-ray diffraction structure of (**4**) as shown in Fig. 1, confirms the structural inferences made on the basis of spectroscopic results, in which both the sulfur atoms are in the open face and bound

Table 2—Selected bond distances (Å) and angles (°) for (**4**)

Bond lengths (Å)	
W(1)-W(2)	2.6527(13)
W(1)-B(1)	2.229(19)
W(1)-B(2)	2.35(2)
W(1)-S(1)	2.452(5)
B(1)-B(2)	1.60(3)
Bond angles (°)	
W(1)-S(1)-W(2)	65.56(13)
W(1)-B(2)-W(2)	68.6(6)
W(1)-B(1)-W(2)	73.1(6)

contiguously. The W-W bond length of 2.6527(13) Å (Table 2) in (**4**) is shorter as compared to that of  $[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]$ . Due to the insertion of two S atoms into the metallaborane cage, a contraction of the metal-metal bond is observed, similar to that observed in diselenamolybdaborane  $[(\eta^5\text{-C}_5\text{Me}_5\text{-Mo})_2\text{B}_4\text{H}_4\text{Se}_2]$  [2.665(2) Å], oxamolybdaboranes<sup>36</sup>  $[(\eta^5\text{-C}_5\text{Me}_5\text{-Mo})_2\text{B}_5(\mu_3\text{-OEt})\text{H}_6\text{R}]$  (R = H: 2.6380(8) Å and *n*-BuO: 2.665(2) Å) and  $[(\text{Cp}^*\text{Mo})_2\text{B}_2\text{S}_2\text{H}_2(\mu\text{-}\eta^1\text{-S})]$  (2.6359(16) Å)<sup>26</sup>, those have a significantly shorter metal-metal bond compared to their parent molecule,  $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$  (2.8085(6) Å)<sup>37</sup>. Thus, combined outlook of the dithiatungstaborane and dithiamolybdaborane clusters revealed a significant shortening of the metal-metal bond length which may be due to the withdrawing electron density effect of sulfur atoms from the cluster. The W-S bond lengths of 2.452(5) Å is slightly shorter than those of related metallathiorboranes compounds<sup>38-40</sup>. As listed in Table 3, the average metal-metal and B-S distances in (**4**) are comparable with those of  $[(\text{Cp}^*\text{Mo})_2\text{B}_2\text{S}_2\text{H}_2(\text{S})]$  and other analogous systems<sup>8,26</sup>. The dihedral angle

Table 3—Selected structural parameters and dihedral angles of (4) and other related compounds

Complexes	sep	<i>d</i> [M-M] (Å)	Avg.[B-S] (Å)	Avg.[B-B] (Å)	Dihedral angle (°) <sup>a</sup>
[(CpCo) <sub>2</sub> B <sub>2</sub> S <sub>2</sub> H <sub>2</sub> ]	8	3.06	1.85	1.76	- <sup>b</sup>
[(Cp*Mo) <sub>2</sub> B <sub>2</sub> S <sub>2</sub> H <sub>2</sub> (S)]	6	2.63	1.95	1.69	161.1 <sup>c</sup>
(Cp*Mo) <sub>2</sub> B <sub>4</sub> H <sub>4</sub> Se <sub>2</sub>	7	2.66	1.92	1.71	161.0
(CpW) <sub>2</sub> B <sub>4</sub> H <sub>4</sub> S <sub>2</sub> (4)	7	2.65	1.85	1.63	158.2

<sup>a</sup> Dihedral angle of M<sub>2</sub>B<sub>4</sub> bicapped tetrahedral geometry.

<sup>b</sup> Not accessible; <sup>c</sup> Dihedral angle of M<sub>2</sub>B<sub>2</sub>S<sub>2</sub> bicapped tetrahedral geometry.

between two tetrahedra of compound (4) is 158°. The skeletal electron pair (sep) count reveals that (4) has 7 sep over the cluster, similar to that of the Mo analogue (3).

#### [(Cp\*Mo)<sub>2</sub>B<sub>3</sub>H<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>S)]

Interestingly, the pyrolysis of the *in situ* intermediate, obtained from [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>MoCl<sub>4</sub>)] and [LiBH<sub>4</sub>.thf], with [HS(CH<sub>2</sub>)<sub>n</sub>SH] (n = 2 or 3) yielded an unknown compound,<sup>38</sup> albeit in low yield, along with the formation of (3) and [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>Mo)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>]. The FAB mass analysis in solution of the unknown compound gives a molecular ion peak at 592, corresponding to [Mo<sub>2</sub>B<sub>3</sub>S<sub>2</sub>C<sub>22</sub>H<sub>39</sub>]. The <sup>11</sup>B NMR spectrum rationalizes the presence of three kinds of boron environments (1:1:1), consisting of two doublets and one broad peak of equal intensity. The upfield chemical shifts at -10.4 and -19.2 ppm account for the interaction of boron with the S atoms. The <sup>1</sup>H NMR shows three equal BH resonances each of intensity one; one Cp\* ligand at 1.83, the methylene protons at 2.10 ppm (supported by <sup>13</sup>C-<sup>1</sup>H HSQC experiment) and the two Mo-H-B protons at -9.84 ppm. Further, the <sup>1</sup>H{<sup>11</sup>B}-<sup>11</sup>B{<sup>1</sup>H} HSQC experiment shows the attachment of both the bridging hydrogens to one boron {δ(<sup>11</sup>B) = -19.2 ppm}. The <sup>13</sup>C spectrum also reveals the presence of one kind of Cp\* and the presence of CH<sub>2</sub>-CH<sub>2</sub> unit (supported by DEPT experiment). The infrared spectrum of the unknown compound shows absorptions for BH and CH vibrations. Unfortunately, all efforts to grow single crystals resulted in weakly diffracting material and no data sets of sufficient quality for resolution of the molecule were obtained. Therefore, in the absence of crystallographic data, the composition of the unknown compound is proposed as [(Cp\*Mo)<sub>2</sub>B<sub>3</sub>H<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>S)]. Although clusters containing methanedithiolato ligand<sup>39-45</sup> are known, to the best of our knowledge ethanedithiolato containing clusters have not been reported earlier.

## Conclusions

A high yield synthesis of dithiamolybdaborane has been achieved by using [HS(CH<sub>2</sub>)<sub>n</sub>SH] (n = 2 or 3) as a potential source of sulfur<sup>46</sup>. Furthermore, on the basis of these studies it is expected that in the future a wide range of metallaheteroborane clusters containing heavier *p*-block elements can be synthesized, which may provide valuable insight into the relationship amongst cage geometries and bonding interaction.

## Supplementary Data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 822001 for compound (4). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk.)

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- 38 MS (FAB) P<sup>+</sup>(max): *m/z* (%) 592 (isotopic pattern for 2Mo, 3B, 2C 2S atoms); <sup>11</sup>B NMR (CDCl<sub>3</sub>, 22 °C, 128 MHz): δ = 111.2 (d, *J*<sub>B-H</sub> = 172 Hz, 1B-H), -10.4 (d, *J*<sub>B-H</sub> = 183 Hz, 1B-H), -19.2 (br, 1B); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C, 400 MHz): δ = 8.62 (partially collapsed quartet (*pcq*), 1BH<sub>1</sub>), 2.10 (s, 2CH<sub>2</sub>), 1.81 (s, 30H, 2Cp\*), 1.38 (*pcq*, 1BH<sub>1</sub>), 1.33 (*pcq*, 1BH<sub>1</sub>), -9.84 (br, 2Mo-*H*-Mo); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22 °C, 100 MHz): 103.7 (s; C<sub>5</sub>Me<sub>5</sub>), 41.5 (s; CH<sub>2</sub>), 12.7 (s; C<sub>5</sub>Me<sub>5</sub>); IR (hexane, cm<sup>-1</sup>): 2962 m, 2873 m (CH); 2492 w, 2470 w (BH).
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