

Synthesis and reactivity of dimolybdathiaborane cluster [(Cp*Mo)₂B₄SH₆] (Cp* = η⁵-C₅Me₅)

KIRAN KUMAR VARMA CHAKRAHARI and SUNDARGOPAL GHOSH*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
e-mail: sghosh@iitm.ac.in

Abstract. Chemistry and reactivity of dimolybdathiaborane, [(Cp*Mo)₂B₄SH₆], **1**, obtained from the reaction of 2-mercaptobenzothiazole, [Cp*MoCl₄] and [LiBH₄.thf], has been explored with dinuclear metal carbonyl [Fe₂(CO)₉]. As a result, reaction of **1** with [Fe₂(CO)₉] yielded heterometallathiaborane, [(Cp*Mo)₂B₄H₆SFe(CO)₃], **2** in good yield. Both the new compounds have been characterized in solution by ¹H, ¹¹B and ¹³C NMR spectroscopy and the structural types were unequivocally established by X-ray crystallographic analysis of compound **2**. Cluster **2** has a bicapped octahedral geometry with the {Fe(CO)₃} fragment occupying one of the high-connectivity cluster vertexes rather than a capping position. Interestingly, cluster **1** undergoes geometric changes (bicapped trigonal bipyramid → bicapped octahedron) on the addition of two-electron {Fe(CO)₃} fragment to **1**.

Keywords. Metallaborane; boranes; organometallic; cluster.

1. Introduction

As part of our ongoing studies on the synthesis of metallaheteroborane and their derivatives,^{1–10} our research group recently synthesized the dimolybdaselenaborane cluster, [(Cp*Mo)₂B₄SeH₅(Ph)]¹¹ in moderate yield. During the course of our studies, it has been observed that the nature of chalcogen plays an important role in the product distribution. Therefore, we intended to investigate the reactivity of the intermediate, generated by the reaction between [Cp*MoCl₄] and [LiBH₄.thf], with other potential chalcogen sources. In this report, we describe the synthesis and characterization of [(Cp*Mo)₂B₄SH₆]. Further, the reactivity of [(Cp*Mo)₂B₄SH₆] was explored with dinuclear metal carbonyl compound, such as [Fe₂(CO)₉], that generated a capped cluster with 8 atoms, [(Cp*Mo)₂B₄H₆SFe(CO)₃], **2**.

2. Experimental

2.1 General procedures and instrumentation

All the operations were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under Argon. MeI was freshly distilled prior to use. All other reagents Cp*H,

[Mo(CO)₆], BuLi, BH₃.thf, 2-mercaptobenzothiazole, LiBH₄ 2.0 M in thf, [Fe₂(CO)₉] (Aldrich) were used as received. [Cp*MoCl₄]¹² was synthesized as reported in literature. Thin-layer chromatography (TLC) was carried out on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl₃, 7.26), while a sealed tube containing [Bu₄N(B₃H₈)] in C₆D₆ (δ_B, ppm, –30.07) was used as an external reference for the ¹¹B NMR. Infrared spectra were obtained on a Nicolet 6700 FT-IR spectrometer. Microanalyses for C, H, and N were performed on Perkin Elmer Instruments series II model 2400.

2.2 Synthesis of **1**

In a flame-dried Schlenk tube [Cp*MoCl₄] (0.5 g, 1.34 mmol) in 10 mL of toluene was treated with 5-fold excess of [LiBH₄.thf] (3.4 mL, 6.7 mmol) at –40°C and allowed to stir at room temperature for 1 h. After removal of toluene, the residue was extracted into hexane and filtered through a frit using Celite. The yellowish-green hexane extract was dried *in vacuo*, extracted with 15 mL of toluene and heated at 80°C with 2-mercaptobenzothiazole C₇H₅NS₂ (0.44 g, 2.68 mmol) for 20 h. The solvent was evaporated *in vacuo*; residue was extracted into hexane and passed through Celite mixed with a small amount of silica gel. After removal

*For correspondence

of solvent from the filtrate, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with hexane:CH₂Cl₂ (95:05 v/v) mixture afforded the following compounds in order of elution: Green [(Cp*Mo)₂B₄SH₆], **1** (0.35 g, 48%) and orange [(Cp*Mo)₂B₅H₉]¹³, (0.12 g, 17%).

1: ¹¹B NMR (128 MHz, CDCl₃, 22°C): δ = 101.1 (*d*, *J*_{B-H} = 140 Hz, 1B), 76.7 (*d*, *J*_{B-H} = 148 Hz, 1B), 40.3 (*d*, *J*_{B-H} = 136 Hz, 1B), 10.1 (*d*, *J*_{B-H} = 166 Hz, 1B); ¹H NMR (400 MHz, CDCl₃, 22°C): δ = 8.91 (br, 1B-H_t), 8.12 (br, 1B-H_t), 3.82 (br, 1B-H_t), 2.01 (s, 30H, Cp*), 1.36 (br, 1B-H_t), -10.41 (br, 2Mo-H-B); ¹³C NMR (100 MHz, CDCl₃, 22°C): δ = 106.4 (s, η⁵-C₅Me₅), 12.0 (s, η⁵-C₅Me₅); IR (hexane, cm⁻¹): 2467 (w) (B-H_t); *Anal. Calc.* for C₂₀H₃₆B₄Mo₂S: C 44.18, H 6.67; found: C 43.68, H 6.14.

2.3 Synthesis of [(Cp*Mo)₂B₄H₆SFe(CO)₃], **2**

A hexane solution of **1** (0.2 g, 0.37 mmol) was added to [Fe₂(CO)₉] (0.13 g, 0.36 mmol) at room temperature and stirred for 6 h, then volatiles were removed *in vacuo* and the resulting brown residue was extracted with hexane, and passed through Celite. The filtrate was concentrated and kept at -40°C to remove [Fe₃(CO)₁₂]. The mother liquor was concentrated, and the residue was chromatographed on silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (9:1) mixture yielded **2** (0.08 g, 30%). The recrystallization from a hexane/CH₂Cl₂ mixture gave pure product in the form of purple crystals of **2**.

2: ¹¹B NMR (128 MHz, CDCl₃, 22°C): δ = 86.7 (*d*, *J*_{B-H} = 133 Hz, 2B), 44.7 (*d*, *J*_{B-H} = 132 Hz, 1B), -5.3 (*d*, *J*_{B-H} = 138 Hz, 1B); ¹H NMR (400 MHz, CDCl₃, 22°C): δ = 8.21 (br, 2B-H_t), 4.72 (br, 1B-H_t), 1.92 (s, 30H, Cp*), 1.36 (br, B-H_t), -14.41 (br, 2Mo-H-B); ¹³C NMR (100 MHz, CDCl₃, 22°C): δ = 214.2, 206.5 (s, CO), 105.4 (s, η⁵-C₅Me₅), 12.2 (s, η⁵-C₅Me₅); IR (hexane, cm⁻¹): 2473 (w) ν(B-H_t), 2009 (s), 1950(s) ν(C-O).

2.4 Single crystal structure determination

Crystal data for **2** was collected and integrated using Bruker Apex II CCD area detector system equipped with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 298 K. The structure was solved by heavy atom methods using SHELXS-97¹⁴ and refined using SHELXL-97.¹⁵ The structure with the atom numbering scheme is shown in figure 1 and the selected bond lengths and angles are listed in table 1.

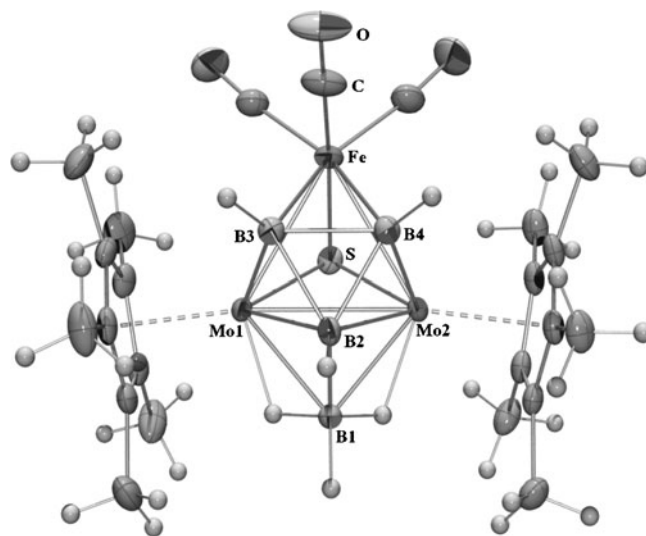


Figure 1. Molecular structure and labelling diagram for [(Cp*Mo)₂B₄H₆SFe(CO)₃], **2**. Thermal ellipsoids have been drawn at the 30% probability level. Selected bond lengths [Å] and angles [deg]: Mo(1)-Mo(2) 2.8846(4), Mo(1)-B(1) 2.259(4), Mo(1)-B(2) 2.317(4), Mo(1)-B(3) 2.124(4), Mo(1)-S(1) 2.3445(9), Mo(1)-Fe(1) 2.7517(6), Fe(1)-S(1) 2.3273(10), B(1)-B(2) 1.775(6), B(2)-B(3) 1.739(6), B(3)-B(4) 1.819(6), B(3)-Fe(1) 2.226(4), B(3)-Mo(1)-B(1) 91.43(15), B(1)-Mo(1)-Fe(1) 106.16(10), B(3)-Mo(1)-Fe(1) 52.42(11), B(2)-Mo(1)-Fe(1) 77.32(10), B(3)-Mo(1)-Mo(2) 75.51(11).

Table 1. Crystal data and structure refinement details for compound **2**.

Empirical formula	C ₂₃ H ₃₆ B ₄ FeMo ₂ O ₃ S, 2
Formula weight	683.55
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	12.0970(7)
<i>b</i> (Å)	16.0863(9)
<i>c</i> (Å)	14.7764(7)
α(°)	90.00
β(°)	107.862(2)
γ(°)	90.00
<i>V</i> (Å ³)	2736.8(3)
<i>Z</i>	4
<i>D</i> _{calc} (Mg/m ³)	1.659
<i>F</i> (000)	1376
μ (mm ⁻¹)	1.525
θ Range (°)	1.92–28.43
Goodness-of-fit	1.260
R1, <i>w</i> R2 [<i>I</i> > 2σ(<i>I</i>)]	0.0282, 0.0684
R1, <i>w</i> R2 (all data)	0.0361, 0.0715
Largest diff. peak, hole (e/Å ³)	0.474, -0.466

3. Results and discussion

3.1 Synthesis and characterization of **1**

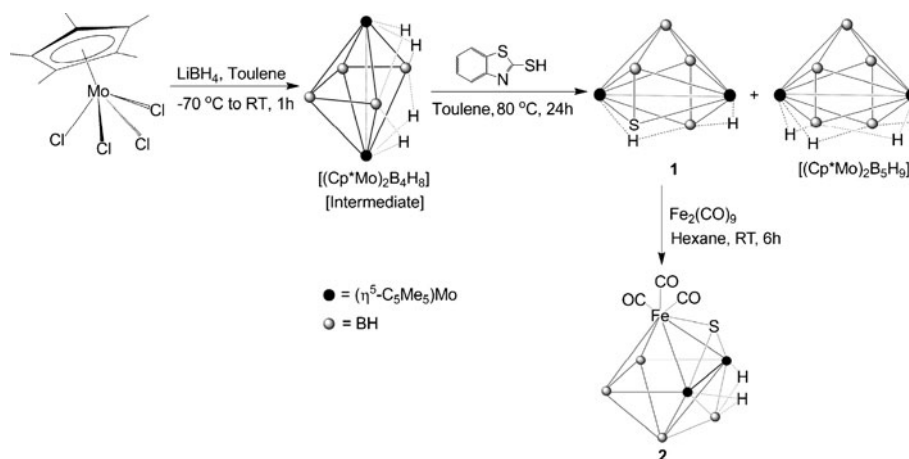
As shown in scheme 1, mild pyrolysis of $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_8]$,¹⁶ a proposed intermediate to $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$, with 2-mercaptobenzothiazole yielded **1**. This reaction also produced few other products, which were observed during the chromatographic work-up, however due to insufficient amounts isolation and characterization was not possible. Interestingly, the isolated yield of compound **1** obtained from 2-mercaptobenzothiazole is enhanced (48%) in comparison with the other chalcogen sources such as, chalcogen powders, dichalcogenide ligands and ethane or propane dithiol.

The composition and structure of **1** was established in comparison of its spectroscopic data with $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SeH}_5(\text{Ph})]$.¹¹ The ^{11}B NMR spectrum indicates the presence of four boron resonances at $\delta = 101.1, 76.7, 40.3$ and 10.1 in an intensity ratio of 1:1:1:1, very similar to $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SeH}_5(\text{Ph})]$ system. The resonance at $\delta = 10.1$ ppm has been assigned to the boron that is attached to sulphur atom. The chemical shift for this particular boron appeared significantly up field region relative to the Se analogue ($\delta = 28.2$). Interestingly, a similar trend has also been observed in $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{E}_2]^2$ system, (E = S, Se, Te). The up-field shift may be due to the electro negativity difference between S and Se. The ^1H NMR spectrum shows the presence of four B-H terminal protons, a single Cp* resonance at $\delta = 2.01$ ppm of relative intensity 30 and Mo-H-B resonance at $\delta = -10.41$ ppm of intensity 2. The ^{13}C NMR spectrum also reveals the presence of one set of Cp* resonance. The IR spectrum of **1** shows a band at 2467 cm^{-1} in a region characteristic of the B-H stretching frequency.

From the elemental analysis combined with the ^{11}B , ^1H and ^{13}C NMR spectroscopic data, **1** is formulated as $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SH}_6]$ and in the absence of crystallographic data, the molecular structure and the spectroscopic properties are best fit with the structure shown in scheme 1. Compound **1** is closely related to $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SeH}_5(\text{Ph})]$, in which the Se and B-Ph groups are replaced by S and B-H, respectively and results in the same number of cluster framework electrons. The compound **1** is best described as a bicapped *closo* trigonal bipyramid $\{(\text{Cp}^*\text{Mo})_2(\text{BH})_3\}$, in which S and BH₃ units are capping the two dissimilar Mo-B-Mo triangular faces.

3.2 Reactivity of **1** with $\text{Fe}_2(\text{CO})_9$

Upon availability of **1** in reasonable quantity, reactivity of **1** was explored with metal carbonyl compounds. The reactions with $[\text{Co}_2(\text{CO})_8]$ led to decomposition of starting material, whereas $[\text{Fe}_2(\text{CO})_9]$ was found accompanied of a compound identified spectroscopically as **2** (scheme 1). Compound **2** has been isolated as orange solid in 30% yield. Three kinds of resonances were observed in the ^{11}B NMR spectrum at $\delta = 86.7, 44.7,$ and -5.3 (2:1:1) and the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum reveals three types of B-H protons in the ratio of 2:1:1 and the presence of one high-field ^1H resonance at $\delta -14.41$ ppm of intensity 2. The ^1H NMR data of **2** suggest a plane of symmetry for a static molecule as well as the presence of single Cp* resonance at 1.92 of relative intensity 30. The ^{13}C NMR spectrum contains signals attributable to the one type of Cp* ligand and $\text{Fe}(\text{CO})_3$ fragment. The IR spectrum of **3** shows a band at 2473 cm^{-1} in a region characteristic of the B-H stretching frequency and two more strong bands at 2009



Scheme 1. Synthesis of dimolybdathiorborane, $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SH}_6]$, **1** and $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_6\text{SFe}(\text{CO})_3]$, **2**.

Table 2. Selected structural parameters and ^{11}B NMR data of **2** and other related compounds.

Compound	sep ^a	$d[\text{M-M}]$ [Å]	Avg. $d[\text{M-B}]$ [Å]	Avg. $d[\text{B-B}]$ [Å]	^{11}B NMR δ ppm	Ref.
$[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SeH}_5(\text{Ph})]$	6	2.81 ^b	2.24	1.74	98.7, 77.5, 42.0, 28.2	11
$[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$	6	2.80 ^b	2.13	1.72	62.9, 25.8	13
$[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_6\text{SFe}(\text{CO})_3]$, 2	7	2.88 ^b	2.23	1.77	86.7, 44.7, -5.3	-
$[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$	7	2.94 ^b	2.27	1.75	90.4, 41.4, 29.7, -0.4	19
$[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$	7	2.93 ^c	2.28	1.79	84.2, 46.2, 39.1, -6.6	20
$[(\text{Cp}^*\text{W})_2\text{B}_6\text{H}_{10}]$	7	2.95 ^c	2.28	1.77	83.9, 47.9, -12.7	20
<i>Closo</i> -2,3-(Cp^*Ru) $_2\text{B}_6\text{H}_3\text{Cl}_3$	7	2.71 ^d	2.17	1.80	119.9, 90.0, 68.2, 66.5, 14.7, -7.7	21

^asep = skeletal electron pair. ^bM=Mo, ^cM=W. ^dM=Ru

and 1950 cm^{-1} which are assigned to the CO stretching modes of the $\text{Fe}(\text{CO})_3$ group. These spectra are consistent with a structure based on a bicapped octahedral cluster as would be expected for addition of a two electron fragment $\text{Fe}(\text{CO})_3$ to a six-sep bicapped trigonal bipyramid, **1**.

Single crystals suitable for X-ray diffraction analysis of **2** were obtained from a hexane/ CH_2Cl_2 solution at -5°C , thus allowing for the structural characterization of **2**. The solid state X-ray structure of **2**, shown in figure 1, is best viewed as a bicapped octahedron $\{\text{Mo}_2\text{B}_4\text{FeS}\}$, with Mo1, Mo2, B2, B3, B4 and Fe occupying the vertices of the core octahedron, in which the faces Mo1-Mo2-Fe and Mo1-Mo2-B2 are capped by S and B1, respectively. The structure and spectroscopic data of **2** is very similar to that of $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$ (M = Mo, W), listed in table 2. The capped BH_3 group in $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$ is substituted by isoelectronic $\mu_3\text{-S}$ and maintains the same number of cluster valency electrons. The change from the bicapped trigonal bipyramidal geometry observed for the six-sep species **1** to the bicapped octahedron observed for **2** is entirely in keeping with the changes predicted by Wade/Mingos rules for the addition of a two-electron three orbital fragment, such as $\text{Fe}(\text{CO})_3$.

The Mo-Mo bond length in **2** is somewhat longer than that found in $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{SeH}_5(\text{Ph})]$ (2.88 Å as opposed to 2.81 Å). The Mo-Fe distances (2.75 and 2.76 Å) are consistent with the existence of a single bond, being somewhat shorter than the corresponding 'unexceptional' distances in $[\text{CpMo}(\text{CO})_2]\text{Fe}(\text{CO})_3$ ($\mu_3\text{-Fe}$) (2.84 Å)¹⁷ and $[(\text{C}_5\text{H}_4\text{Me})\text{MoS}_2\text{Fe}(\text{CO})_3]_2$ (2.85 Å)¹⁸ and being similar in length to that found in $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$.¹⁹

Both the clusters **1** (6 sep) and **2** (7 sep) appear to follow the regular electron counting rules, appropriate for bicapped trigonal bipyramid and bicapped octahedral structures, respectively. The seven-sep bicapped

octahedral architecture of **2** satisfies the electron counting rules derived from the borane analogy. There are only few examples of metallaboranes with bicapped octahedral geometry known, $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3]$ (M = Mo, W), $[(\text{Cp}^*\text{W})_2\text{B}_6\text{H}_{10}]$,^{19,20} *closo*-2,3-(Cp^*Ru) $_2\text{B}_6\text{H}_3\text{Cl}_3$ ²¹ and $\text{Cp}_3^*\text{Ru}_2\text{IrB}_5\text{H}_5$.²² As per our knowledge **2** is the first example of metallaheteroborane with bicapped octahedral geometry.

4. Conclusions

Dimolybdathiaborane **1** has been synthesized very efficiently from a different type of sulphide source. Isolation of dimolybdathia and selenaborane clearly indicates insertion of group 16 elements other than oxygen should be feasible. Further, isolobal analogy also allows us to investigate the insertion of group 15 elements in metallaborane core. Such work is under process in our laboratory. Although there are only few examples of metallaboranes with bicapped octahedral geometry known, as per our knowledge cluster **2** is the first example of metallaheteroborane with bicapped octahedral geometry.

Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 831354 for compounds **2**. 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; or e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html.

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