Direct insertion of sulfur, selenium and tellurium atoms into metallaborane cages using chalcogen powders

Satyanarayan Sahoo [a], Shaikh M. Mobin [b], Sundargopal Ghosh [a,*]

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
[b] National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Mumbai 400 076, India

ABSTRACT

Reaction of $[(\eta^5\text{-}C_5Me_5)MCl_4]$, **1–2** (**1**: M = Mo and **2**: W) with six fold excess of [LiBH$_4$·thf] followed by thermolysis with excess chalcogen powders (S, Se and Te) yielded dichalcomolybda- and tungstaboranes, $[(\eta^5\text{-}C_5Me_5M)_2B_4H_4E_2]$, **5–8** (**5**: M = Mo, E = S; **6**: M = Mo, E = Se; **7**: M = Mo, E = Te; **8**: M = W, E = Se) in modest yields. The geometry of **5–8** resembles a hexagonal bipyramid with a missing connectivity of two chalcogen vertices and a very short cross cage metal–metal bonding. All these new dichalcometalla-boranes have been characterized by mass, ^{1}H, ^{11}B, ^{13}C NMR spectroscopy, and the structural types were unequivocally established by crystallographic analysis of compound **6**.

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1. Introduction

An area of ongoing importance in polyhedral metallaborane chemistry is the progress of new efficient methods in which atom-insertion reactions leading to expanded-cage or mixed clusters may be accomplished. Although the structural diversity 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 by carboranes [1–6] and metallacarboranes [7–14]. Apart from the carboranes and metallacarboranes, the most wide-ranging main-group polyhedral heteroboranes are thiaboranes and thiametalla-boranes. By contrast, polyborane-based boron containing clusters that also contain other group 16 elements as a cluster constituent are less [15–25].

Most of the polyhedral metallaheteroborane compounds have been synthesized from the reaction of metal center with pre-formed polyhedral heteroborane substrates [26–35]. On the other hand, the converse synthetic approach, that is, the reaction of het-ero atom with pre-formed polyhedral metallaborane substrates, is not well documented [36–40]. Recently, we have revealed that the reaction of $[(\eta^5\text{-}C_5Me_5)MoCl_4]$ with [BH$_3$·thf] led to the isolation of two eight-vertex oxamolybdaborane clusters [41], $[(\eta^5\text{-}C_5Me_5\text{-}Mo)_2B_5(\mu_3\text{-}OEt)H_6R]$ (R = H and *n*-BuO), thus, metallaheterobor-anes containing group 16 elements, other than oxygen, became of interest. In this paper we report a new, straightforward, chalco-gen atom-insertion reaction that has allowed the production of a novel *nido*-$[(\eta^5\text{-}C_5Me_5M)_2B_4H_4E_2]$ (M = Mo and W and E = S, Se and Te) cluster system.

## 2. Results and discussion

2.1. Synthesis and characterization of dichalcomolybdaborane clusters, $[(\eta^5\text{-}C_5Me_5Mo)_2B_4H_4E_2]$ (**5**: E = S; **6**: E = Se)

Reaction of $[(\eta^5\text{-}C_5Me_5)MoCl_4]$, **1** with a six fold excess of [LiBH$_4$·thf] for 1 h, followed by thermolysis with chalcogen powders (S and Se) in toluene at 100 °C for 30 h yielded orange crystal-line dithiamolybdaborane, $[(\eta^5\text{-}C_5Me_5Mo)_2B_4H_4S_2]$, **5** and diselenamolybdaborane, $[(\eta^5\text{-}C_5Me_5Mo)_2B_4H_4Se_2]$, **6** in modest yields (Scheme 1). All the reactions were monitored by ^{11}B NMR spectroscopy, which revealed formation of the new boron contain-ing compounds, as indicated by the presence of two resonances in the ^{11}B{^{1}H} NMR spectrum at δ = −10 to 85 ppm region. Beside the formation of metallaheteroboranes **5** or **6**, one known compound $[(\eta^5\text{-}C_5Me_5Mo)_2B_5H_9]$, **3** has been isolated in both the cases as a major product [42]. Descriptions of the characterizations of **5** and **6** from IR, ^{1}H, ^{11}B, ^{13}C NMR, mass spectroscopy and X-ray diffrac-tion studies (for **6** only) follow.

The composition of **5** is defined by the FAB mass spectrometry and isotopic distribution pattern characteristics of four boron, two molybdenum and two sulfur atoms. The ^{11}B NMR spectrum shows two boron resonances at δ = 81.8 and −4.1 ppm with equal intensity. The ^{1}H NMR shows the presence of four B–H terminal protons (1:1) and one kind of Cp* ligand at δ = 1.94 ppm
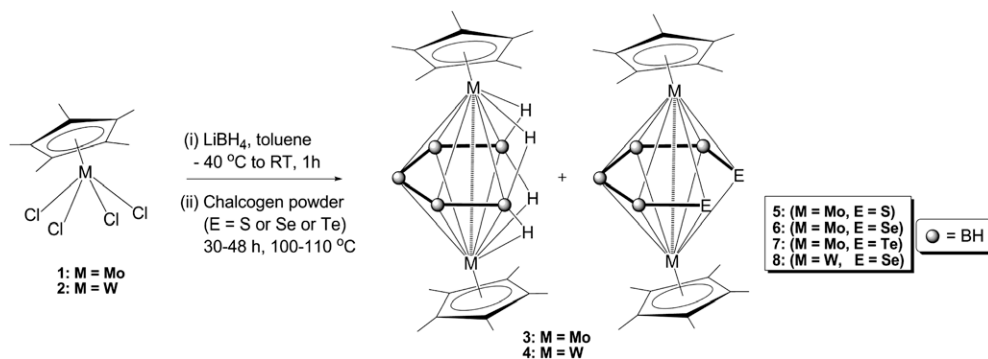
Scheme 1.

($Cp^* = \eta^5\text{-}C_5Me_5$). From the mass spectral analysis combined with the ^{11}B, ^1H and ^{13}C NMR spectra, **5** is formulated as ($\eta^5\text{-}C_5Me_5\text{-}Mo)_2B_4H_4S_2$. The composition and structure of **5** is established in comparison of its spectroscopic data with **6** as discussed below.

The diselenamolybdaborane, **6** has been isolated in ~25% yield from the reaction mixture. The mass spectrum of **6** is consistent with a formula containing four B, two Mo and two Se atoms and the parent ion mass of 668 which corresponds well with the replacement of two S atoms in **5** by two Se atoms. The ^{77}Se NMR shows a single resonance at $\delta = -23$ ppm which indicates that both the Se atoms are in equivalent positions. The ^1H and ^{13}C NMR chemical shift values are comparable to those of **5**. The sharp ^{11}B NMR resonance at $\delta = 4.2$ ppm has been assigned to the boron attached to selenium atoms. The spectrum of **6** is very similar to that of **5**, it differs only in the chemical shift of those boron atoms attached to Se. Furthermore, the $^1H\{^{11}B\}$ NMR spectrum of **6** shows one type of Cp^* at $\delta = 1.92$ ppm and two types of B–H protons at $\delta = 9.36$ and 4.25 ppm. The single crystal X-ray diffraction structure of **6**, shown in Fig. 1, confirms the structural inferences made on the basis of spectroscopic results.

As shown in Fig. 1 both the selenium atoms in **6** are in the open face, and bound contiguously to one boron atom and two molybdenum metals. The Mo–Mo bond length of 2.665(2) Å in **6** is significantly shorter than that observed in **3** {2.8085(6) Å} [43]. The significant shortening of the Mo–Mo bond length might arise from

the effect of the selenium atoms which withdraw electron density from the cluster. The boron–selenium bond lengths, B1–Se1 and B4–Se2, are equal, 1.92 and 1.93 Å, respectively. However, they are significantly shorter as compared to those observed in other selenaborane clusters [16,19,23,24]. This may be due to the tendency of boron and selenium atoms to form polarized bonds that have a localized two-center character resulting in the observed distances [44,45].

2.2. Synthesis and characterization of dichalcomolybda- and tungstaborane clusters, [(η^5-C$_5$Me$_5$M)$_2$B$_4$H$_4$E$_2$] (7: M = Mo, E = Te; 8: M = W, E = Se)

As shown in Scheme 1, reaction of **1** or **2** with a six fold excess of [LiBH$_4$·thf] for 1 h, followed by thermolysis in presence of excess of Te or Se powders at 110 °C for 2 days yielded orange crystalline ditelluramolybdaborane, [(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_4$Te$_2$], **7** and diselena-tungstaborane, [(η^5-C$_5$Me$_5$W)$_2$B$_4$H$_4$Se$_2$] **8**, relatively in less yields. As discussed above, these reactions were also monitored by ^{11}B NMR spectroscopy, which revealed the development of the new compounds, similar to those of **5** and **6**, as indicated by the presence of two similar ^{11}B resonances. Descriptions of the characterizations of **7** and **8** from IR and multinuclear NMR spectroscopy follow.

Compounds **7** and **8** have been characterized in comparison of its spectroscopic data with **5** and **6**. The ^{11}B chemical shift values of **7** and **8** (two resonances in the ratio 1:1) are in good agreement with those of **5** and **6** and suggest the structures, if static, of higher symmetry. Consistent with this observation, both **7** and **8** show one kind of Cp^* signal and presence of no MoHB protons. In the absence of crystallographic data, the molecular formula of **7** and **8** and its spectroscopic properties are best fit with the structure shown in Scheme 1.

2.3. Discussion

Notably, the pathway for the formation of **5–7** has not been established; however, note that during the metathesis reaction of [(η^5-C$_5$Me$_5$)MoCl$_4$] with borohydrides, [(η^5-C$_5$Me$_5$Mo)$_2$B$_5$H$_8$] has been proposed as an intermediate species leading to [(η^5-C$_5$Me$_5$-Mo)$_2$B$_5$H$_9$] [46]. Therefore, compounds **5–7** have been postulated to be generated by the insertion of two chalcogen atoms into the core geometry of [(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_8$] with the elimination two molecules of H$_2$ (Scheme 2). Since a cage chalcogen atom is a four-skeletal-electron donor (isoelectronic with BH^{2-}), the incorporation of two chalcogen atoms into a boron cage necessitates the formation of open cage geometries. An attempt to isolate the *closed* analogs of [(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_4$E$_2$] from the reaction
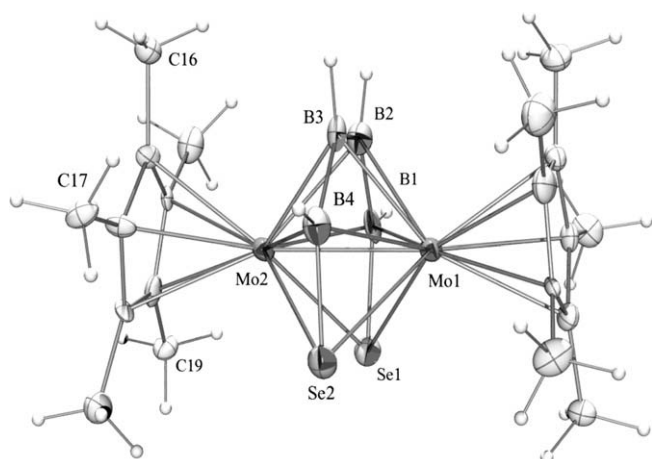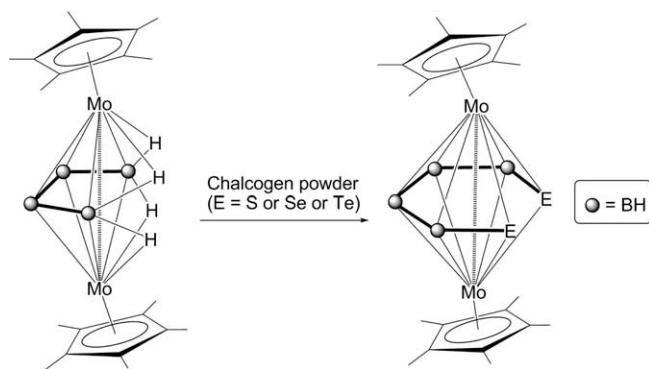

Fig. 1. Molecular structure of [(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_4$Se$_2$], **6**. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.665(2), Mo(1)–B(1) 2.39(2), Mo(1)–B(3) 2.26(2), Mo(2)–B(1) 2.38(2), Mo(2)–B(3) 2.29(2), B(1)–B(2) 1.67(3), B(2)–B(3) 1.71(3), B(3)–B(4) 1.75(3), B(1)–Se(1) 1.92(3), B(4)–Se(2) 1.93(3), Mo(1)–Se(1) 2.590(3), Mo(2)–Se(1) 2.579(3); Mo(1)–B(1)–Mo(2) 68.0(7), Mo(1)–B(3)–Mo(2) 71.8(7), Mo(1)–Se(1)–Mo(2) 62.08(7).

Scheme 2. Proposed mechanism for the formation of dichalcomolybdaboranes, **5–7**.

mixture of [(η⁵-C₅Me₅)MoCl₄], borane reagents, [LiBH₄·thf] or [BH₃·thf], and chalcogen powders has been unsuccessful.

Superficially the core geometry of **6** resembles that of a hexagonal bipyramid with a missing connectivity of two vertices (Se1 and Se2 in Fig. 1) and a short cross cage Mo–Mo bond (2.665(2) Å). Alternatively, as the available cluster bonding electrons of **6** are insufficient to meet the requirements of single eight-vertex *nido*-geometry, it could be better described as 26 valence electron (ve) triple-decker complex [47–50]. In addition, **6** is isoelectronic to those of arene-bridged-[(η⁵-C₅H₅V)₂(μ-η⁶:η⁶-C₆H₆)] [51], triple-decker sandwich complexes, for example, [(η⁵-C₅Me₄EtV)₂(μ-η⁶:η⁶-P₆)] [52] and [(η⁵-C₅H₃ᵗBu₂Nb)₂(μ-η⁶:η⁶-P₆)] [53], and *closo*-[(η⁵-C₅Me₅W)₂B₆H₁₀] [54]. The distance between two selenium atoms (Se1 and Se2 in Fig. 1) in **6** is 3.16 Å, much longer than an average Se–Se bond distance {2.29–2.39 Å} [55–57]. By analogy with **5–6**, compounds **7** and **8** can be considered as 50-electron, electronically unsaturated dichalcometallaboranes where both the chalcogen atoms bound contiguously to one boron and two metal centers.

The transition metals (Mo and W) as well as the chalcogen elements (S, Se and Te), play an essential role in the production of dichalcometallaborane compounds **5–8**. As a result, it is observed that for the development of **7** and **8** it requires longer reaction time and relatively drastic reaction conditions than those applied for **5** and **6**.

3. Conclusions

An efficient and straightforward synthesis of [(η⁵-C₅Me₅M)₂-B₄H₄E₂], **5–8** (**5**: M = Mo, E = S; **6**: M = Mo, E = Se; **7**: M = Mo, E = Te and **8**: M = W, E = Se) has been discovered by the reaction between an intermediate, generated from the reaction of [(η⁵-C₅Me₅)MCl₄], **1–2** and [LiBH₄·thf]; and chalcogen powders (S, Se or Te). The direct insertion of chalcogen atoms into molybda- and tungstaborane frameworks illustrates that chalcogen atom insertion can be built on other metallaborane fragments under the same or different reaction conditions. Furthermore, this new synthetic route represents an exciting development in metallaborane chemistry, which would make it possible to synthesize metallaheteroboranes not doable by other available methods. Efforts to assess the scope, limitations, and synthetic applications of this method, as well the detail mechanistic study, are now in process.

4. Experimental

4.1. 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. Cp*H, Mo(CO)₆, W(CO)₆, BuLi, [BH₃·thf], [LiBH₄·thf], chalcogen powder (E = S, Se and Te) (Aldrich) were used as received. MeI purchased from Aldrich and freshly distilled prior to use. [(η⁵-C₅Me₅)MCl₄] (M = Mo and W) were prepared with some modification [58] of Green [59] work. The external reference, [Bu₄N(B₃H₈)] [60], for the ¹¹B NMR was synthesized with the literature method. Chromatography was carried out on 3 cm of silica gel in a 2.5 cm dia column. Thin layer chromatography was carried 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, benzene, 7.16), while a sealed tube containing [Bu₄N(B₃H₈)] in C₆D₆ (δB, ppm, −30.07) was used as an external reference for the ¹¹B NMR. Ph₂Se₂ was used as an external reference (δSe, ppm, 454) for the ⁷⁷Se NMR. Infrared spectra were obtained on a Nicolet 6700 FT-IR spectrometer. Mass spectra were obtained on a Jeol SX 102/Da-600 mass spectrometer/Data System using Argon/Xenon (6 kV, 10 mÅ) as the FAB gas.

4.2. General procedure for the synthesis of [(η⁵-C₅Me₅Mo)₂B₄H₄E₂], 5–6 (5: E = S; 6: E = Se)

To [(η⁵-C₅Me₅)MoCl₄], (0.5 g, 1.34 mmol) in 20 mL of toluene was added sixfold excess of [LiBH₄·thf] (4.03 mL, 8.05 mmol) at −40 °C. The mixture was stirred at room temperature for 1 h. 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 sixfold excess of chalcogen powders (for S powder, 0.26 g, 8.05 mmol and for Se powder, 0.64 g, 8.05 mmol) for 30 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 filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with hexane yielded orange yellow (η⁵-C₅Me₅Mo)₂B₄H₄S₂, **5** (0.08 g, 10%) and orange red (η⁵-C₅Me₅Mo)₂B₄H₄Se₂, **6** (0.22 g, 25%), based on S and Se powder respectively.

[(η⁵-C₅Me₅Mo)₂B₄H₄S₂], 5: MS (FAB) P⁺(max): m/z (%) 574 (isotopic pattern for 2Mo, 2S and 4B atoms); ¹¹B NMR (400 MHz, [d₆] benzene, 22 °C): δ = 81.8 (br, 2B), −4.1 (br, 2B); ¹H NMR (400 MHz, [d₆] benzene, 22 °C): δ = 9.35 (partially collapsed quartet (*pcq*), 2BHₜ), 4.12 (*pcq*, 2BHₜ), 1.94 (s, 30H, Cp*); ¹³C NMR (400 MHz, [d₆] benzene, 22 °C): δ = 108.8 (s, η⁵-C₅Me₅), 13.7 (s, η⁵-C₅*Me₅*); IR (hexane, cm⁻¹): 2490w (B–Hₜ); Anal. Calc. for ¹²C₂₀¹H₃₄⁹⁶Mo₂¹¹B₄³²S₂: C, 41.87; H, 5.97. Found: C, 39.92; H, 5.67%.

[(η⁵-C₅Me₅Mo)₂B₄H₄Se₂], 6: MS (FAB) P⁺(max): m/z (%) 668 (isotopic pattern for 2Mo, 2Se and 4B atoms); ¹¹B NMR (400 MHz, [d₆] benzene, 22 °C): δ = 81.8 (d, J_{B–H} = 151 Hz, 2B), 4.2 (d, J_{B–H} = 149 Hz, 2B); ¹H NMR (400 MHz, [d₆] benzene, 22 °C): δ = 9.36 (partially collapsed quartet (*pcq*), 2BHₜ), 4.25 (*pcq*, 2BHₜ), 1.92 (s, 30H, Cp*); ¹³C NMR (400 MHz, [d₆] benzene, 22 °C): δ = 108.1 (s, η⁵-C₅Me₅), 14.2 (s, η⁵-C₅*Me₅*); ⁷⁷Se NMR (500 MHz, [d₆] benzene, 22 °C): δ = −23 (s, 2Se); IR (hexane, cm⁻¹): 2486w (B–Hₜ).

4.3. Synthesis of [(η⁵-C₅Me₅Mo)₂B₄H₄Te₂] (7)

To [(η⁵-C₅Me₅)MoCl₄], (0.5 g, 1.34 mmol) in 20 mL of toluene was added sixfold excess of [LiBH₄·thf] (4.03 mL, 8.05 mmol) at −40 °C and stirred at room temperature for 1 h. After removal of toluene the residue was extracted with hexane. The hexane extract was filtered through a frit using Celite, dried and taken in 25 mL of toluene. The toluene solution was heated at 110 °C with an eightfold excess of Te powder (1.37 g, 10.73 mmol) for 2 days. 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 filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with hexane yielded orange [(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_4$Te$_2$], **7**, (0.08 g, 8%).

[(η^5-C$_5$Me$_5$Mo)$_2$B$_4$H$_4$Te$_2$], **7**: ^{11}B NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 81.3$ (d, $J_{B-H} = 151$ Hz, 2B), 11.6 (d, $J_{B-H} = 144$ Hz, 2B); ^{1}H NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 9.27$ (partially collapsed quartet (*pcq*), 2BH$_t$), 4.36 (*pcq*, 2BH$_t$), 1.93 (s, 30H, Cp*); ^{13}C NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 107.5$ (s, η^5-C$_5$Me$_5$), 15.1 (s, η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2488w (B–H$_t$); Anal. Calc. for ^{12}C$_{20}$^{1}H$_{34}$^{96}Mo$_2$^{11}B$_4$^{128}Te$_2$: C, 31.41; H, 4.48. Found: C, 29.96; H, 4.22%.

4.4. Synthesis of [(η^5-C$_5$Me$_5$W)$_2$B$_4$H$_4$Se$_2$] (**8**)

To [(η^5-C$_5$Me$_5$)WCl$_4$], (0.1 g, 0.22 mmol) in 20 mL of toluene was added sixfold excess of [LiBH$_4$·thf] (0.65 mL, 1.3 mmol) at −40 °C. The mixture was stirred at room temperature for 1 h. After removal of toluene the residue was extracted with hexane and filtered through a frit using Celite. The light brown hexane extract was dried and taken in 25 mL of toluene and heated at 110 °C with an eightfold excess of Se powder (0.14 g, 1.74 mmol) for 2 days. 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 filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with hexane yielded orange [(η^5-C$_5$Me$_5$W)$_2$B$_4$H$_4$Se$_2$], **8** (0.01 g, 5%).

[(η^5-C$_5$Me$_5$W)$_2$B$_4$H$_4$Se$_2$], **8**: ^{11}B NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 70.7$ (d, $J_{B-H} = 153$ Hz, 2B), −0.4 (d, $J_{B-H} = 173$ Hz, 2B); ^{1}H NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 8.39$ (partially collapsed quartet (*pcq*), 2BH$_t$), 4.17 (*pcq*, 2BH$_t$), 2.14 (s, 30H, Cp*); ^{13}C NMR (400 MHz, [d_6] benzene, 22 °C): $\delta = 105.7$ (s, η^5-C$_5$Me$_5$), 14.5 (s, η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2498w (B–H$_t$).

Note that *nido*-(η^5-C$_5$Me$_5$Mo)$_2$B$_5$H$_9$, **3** and *nido*-(η^5-C$_5$Me$_5$W)$_2$B$_5$H$_9$, **4** have been isolated in respective Mo and W systems and characterized in comparison of its spectroscopic data reported earlier by Aldridge and Weller, et al., respectively [42,61].

4.5. X-ray Structure Determination

Suitable X-ray quality crystals of **6** were grown by slow diffusion of a hexane:CH$_2$Cl$_2$ (9.5:0.5 *v/v*) solution and single crystal X-ray diffraction studies were undertaken. Crystal data for **6** was collected and integrated using OXFORD DIFFRACTION XCALIBUR-S CCD system equipped with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 150 K. The structure was solved by heavy atom methods using SHELXS-97 and refined using SHEL-XL-97 (Sheldrick, G.M., University of Göttingen). The molecular structures were drawn using ORTEP-3. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens could be located in the difference Fourier map. However, the hydrogen atoms bonded to carbons and borons were fixed at chemically meaningful positions and were allowed to ride with the parent atom during the refinement.

Crystal data for **6**: formula, C$_{20}$H$_{34}$B$_4$Mo$_2$Se$_2$; crystal system, space group: triclinic, $P\bar{1}$. Unit cell dimensions: $a = 9.567(4)$ Å, $\alpha = 75.98(3)$°; $b = 10.777(4)$ Å, $\beta = 85.96(3)$°; $c = 12.026(4)$ Å, $\gamma = 88.69(3)$°; $Z = 2$. Density (calculated) 1.847 Mg/m^3. Final R indices [$I > 2\sigma(I)$], $R_1 = 0.0872$, $wR_2 = 0.2155$. Index ranges: $-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$. Crystal size $0.23 \times 0.18 \times 0.15$ mm^3. Reflections collected 12 106, independent reflections 5449, [$R_{int} = 0.1279$], Goodness-of-fit (GOF) on F^2 0.935.

Supplementary material

CCDC 745423 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.

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