



Substitution at boron in molybdaborane frameworks: Synthesis and characterization of isomeric $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{X}_m$ (when X = Cl: $n = 5, 7, 8$; $m = 4, 2, 1$ and X = Me: $n = 6, 7$; $m = 3, 2$)

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ABSTRACT

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ with 6-fold excess of $\text{LiBH}_4\cdot\text{thf}$ followed by pyrolysis with $\text{BHCl}_2\cdot\text{SMe}_2$ in toluene at 90°C yielded known $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$ (**1**) and B-Cl inserted $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_8\text{Cl}$ (**2**), $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$ (**3–5**, three isomers) and $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_5\text{Cl}_4$ (**6**). In addition, reaction of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$ with 5-fold excess of $n\text{-BuLi}$ followed by excess of MeI in THF yielded B-Me inserted metallaboranes $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7(\text{CH}_3)_2$ (**7, 8** two isomers) and $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_6(\text{CH}_3)_3$ (**9, 10** two isomers). Isolated yields of **2–6** are poor but **7–10** are modest to good. Compounds **2–10** can be viewed as bicapped *closo* trigonal bipyramidal geometry. All the new compounds have been characterized in solution by IR, ^1H , ^{11}B , ^{13}C NMR and mass spectroscopy as simple substitution derivatives of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$ and the structural types were unequivocally established by crystallographic analysis of compounds **2, 3, 5** and **6**.

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1. Introduction

Electrophilic substitution of cage B-H terminal bonds in polyhedral boranes and carboranes have been elegantly demonstrated by Hawthorne [1–5]. Such studies, [6–21] including those leading to peralkylation, perhydroxylation, or perhalogenation, continue to be of significant interest as the persubstituted borane or carborane clusters bear potential applicability in several areas as targets for anti tumor activity [22], weakly coordinating anion [23], components of radioimaging reagent [24], space-controlling drug component, [25]. Further, derivative chemistry has been shown to be crucial in some instances, e.g., modification of the reactivity of carborane fragments such that multiple stacking reactions are possible [26,27].

The *exo*-cluster substitution chemistry in metallaboranes differs considerably from those of pure boranes and carboranes and the absence of useful synthetic routes to metallaboranes and any systematic derivative chemistry has inhibited the development of these compounds. However, availability of good synthetic routes to metallaboranes of group 5–9 [28–30] and a recent study by Hawthorne's group on *exo*-cluster substitution, [3,4,31,32] led us to explore the development of routes of B-functionalized metallaborane species. Introduction of substituents on the boron in metallaboranes is important if one wishes to make complexes that are

resistant to deboronation (decapitation) by electrophiles [33–36]. Further, halogenation of metallaborane clusters has specific interest, since they are important in preparing functionalized clusters for assembly into larger arrays, extended polymetallic clusters [37], and B-B linked systems [38–41]. Considering the utility of halogenated metallaboranes, improved methods for their preparation would contribute to their utility.

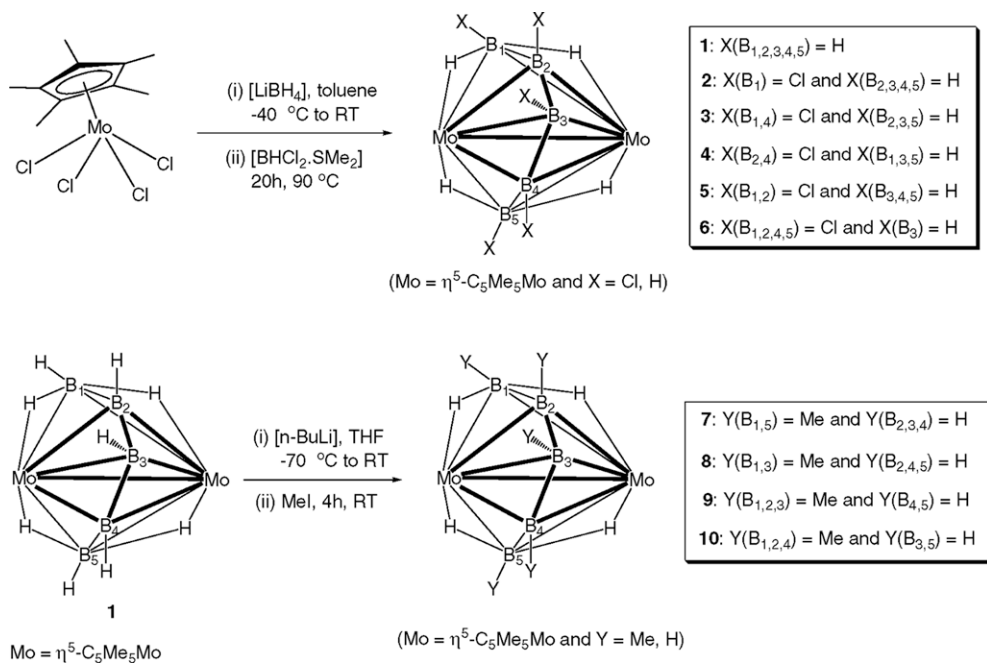
Although few reports available on the chlorination of boron on metallaboranes [42–45], it is not yet clear what factors actually dominates the substitution chemistry. Therefore, it is desirable to have systematic and efficient methods for achieving B-peralkylation or B-perhalogenation of metallaborane compounds. In the following we present the results of reaction between $(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ and $\text{LiBH}_4\cdot\text{thf}$, followed by pyrolysis with $\text{BHCl}_2\cdot\text{SMe}_2$ to afford B-Cl inserted **2–6**. We have also investigated the action of methyl iodide as an agent for B-methylation on the molybdaborane, $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$, **1** which led to the isolation of methylated derivatives, **7–10**.

2. Result and discussion

2.1. Synthesis and characterization of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Cl}_m$ ($n = 5, 7, 8$; $m = 4, 2, 1$)

As shown in Scheme 1, a room temperature reaction of purple $(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ with 6-fold excess of $\text{LiBH}_4\cdot\text{thf}$ for 1 h followed by 6-fold excess of $\text{BHCl}_2\cdot\text{SMe}_2$ in toluene at 90°C for 20 h resulted

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Scheme 1. Synthesis of B-chlorinated and B-methylated molybdaborane derivatives.

in the formation five B-Cl inserted metallaborane products, **2–6**. The reactions were monitored by ^{11}B NMR spectroscopy, which revealed formation of new boron containing compounds, as indicated by resonances in the ^{11}B NMR spectrum at $\delta = 80\text{--}20$ ppm. Descriptions of the characterizations of **2–6** from IR, ^1H , ^{11}B , ^{13}C NMR, mass spectroscopy and X-ray diffraction studies follow.

Metallaborane **2** has been characterized by mass, NMR, and with an X-ray diffraction study. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows three types of BH and one type of B-Cl environment in a ratio of 1:2:1:1. The resonance at $\delta = 37.91$ ppm showed no coupling in $^{11}\text{B}\{^1\text{H}\}$ NMR confirms the B-Cl environment and the resonance at $\delta = 57.7$ ppm is an accidental overlap of two ^{11}B resonances. From the mass spectral analysis combined with the ^{11}B NMR spectrum, **2** is formulated as $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_8\text{Cl}$. Furthermore, the decouple $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum shows one type of Cp^{*} protons (where Cp^{*} = $\eta^5\text{-C}_5\text{Me}_5$), three types of B-H protons in the ratio of 1:1:2, and two types of Mo-H-B protons at $\delta = -5.93$ and -6.84 ppm.

The molecular structure of **2**, determined by a single-crystal X-ray diffraction study, is shown in Fig. 1. Its geometry is similar to that of $(\eta^5\text{-C}_5\text{Me}_5\text{M})_2\text{B}_5\text{H}_9$, (M = Cr, Mo, W) [46–48] and is best described as a bicapped *closo* trigonal bipyramid. The Mo–Mo, avg. B–B and avg. Mo–B bond distances of 2.81, 1.73, and 2.26 Å in **2** are comparable with that of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$.

A second set of products, **3–5**, have been isolated in yields of 10%, 6% and 8% respectively. All the spectroscopic data show that compounds **3–5** are geometrical isomers differing only in the position of the Cl and H atom. The mass spectra of **3–5** are consistent with a formula containing five B, two Mo and two Cl atoms and the parent ion mass of 594 corresponds to substitution of two B-H terminal hydrogens in **1** by chlorine. The ^{11}B NMR spectrum of **3** shows five resonances with an intensity ratio of 1:1:1:1:1. Two sharp resonances at $\delta = 68.6$ and 38.5 ppm have been assigned to the boron atoms attached to chlorine. The single crystal X-ray diffraction structure of **3**, shown in Fig. 2, confirms the structural inferences made on the basis of spectroscopic results. The Mo–Mo distance of 2.8276(4) Å in **3** is slightly longer than the Mo–Mo distance of 2.8144 (7) Å in **2**.

The composition and structure of **4** is established in comparison of its spectroscopic data with **3**. The FAB mass analysis of **4** gives a molecular ion at 594 corresponding to $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$. This formulation of compound **4** rationalized the presence of three kinds of boron environment in the ratio of 2:1:2. A sharp resonance at $\delta = 70.36$ ppm showed no coupling in $^{11}\text{B}\{^1\text{H}\}$ NMR confirms two B-Cl environments. Similarly, the decouple $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum reveals three types of B-H protons in the ratio 1:1:1, and presence one kind of Mo-H-B protons at $\delta = -6.41$ ppm. The molecular formulas as well as the spectroscopic properties of **4** are best fit with the structure as shown in Scheme 1.

Compound **5** has been isolated following thin layer chromatography (TLC) in 8% yield and characterized spectroscopically and with an X-ray structure determination. The FAB mass analysis of **5** gives a molecular ion peak corresponding to $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$. The ^{11}B NMR spectrum indicates the presence of a five boron environments in 1:1:1:1:1 intensity ratio and $^{11}\text{B}\{^1\text{H}\}$ NMR suggests three types of BH and two types of B-Cl environments. The single crystals suitable for X-ray diffraction analysis of **5** were obtained from a hexane solution at -10 °C. The molecular structure of **5** shown in Fig. 3 is consistent with the observed spectroscopic data. The Mo–B and B–B bond distances are identical to those observed in **2** and **3**.

Compound **6** has been isolated in 4% yield. The mass spectroscopic measurement of **6** gives a molecular ion corresponding to $\text{C}_{20}\text{H}_{35}\text{B}_5\text{Mo}_2\text{Cl}_4$. Both ^{11}B NMR and ^1H NMR spectra of **6** indicate a highly symmetrical molecule. The ^{11}B NMR spectrum shows three types of boron resonances in the ratio of 2:2:1. The resonances at $\delta = 66.03$ and 36.61 ppm showed no coupling in $^{11}\text{B}\{^1\text{H}\}$ NMR which confirms the presence of four B-Cl environments. The solid state X-ray structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_5\text{Cl}_4$, **6**, shown in Fig. 4, has a bicapped *closo* trigonal bipyramidal geometry and isostructural with **2**, **3** and **5**. Compound **6** is the most chlorinated among **2–6**. The Mo–B bond lengths of **6** range from 2.21 Å to 2.33 Å and the B–B distances range from 1.70 Å to 1.77 Å and similar to those observed in **2**, **3**, and **5**. The Mo–Mo bond distance of 2.8441(3) Å in **6**, which is tetrachloro substituted, is the longest however, a shortest Mo–Mo distance of 2.8144(7) Å is observed in monochloro derivative, that is **2**.

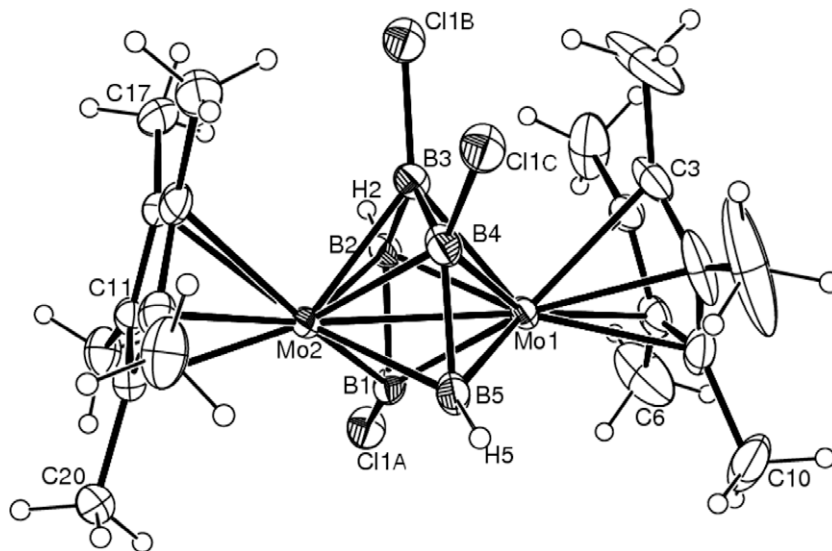


Fig. 1. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_8\text{Cl}$ (**2**). The chlorine atom attached to the boron is disordered over three orientations (Cl1A, Cl1B and Cl1C) in the ratio of 0.66:0.12:0.21, respectively. Selected bond lengths (Å) and angles ($^\circ$): Mo(1)–Mo(2) 2.8144(7), Mo(1)–B(1) 2.302(7), Mo(1)–B(2) 2.221(8), Mo(1)–B(5), 2.327(8), Mo(2)–B(1) 2.314(7), Mo(2)–B(2) 2.219(8), Mo(2)–B(5) 2.334(8), B(1)–B(2) 1.754(11), B(3)–B(4) 1.705(13), B(4)–B(5) 1.752(12), B(1)–Cl(1A) 1.812(8), Mo(1)–B(1)–Mo(2) 75.1(2), Mo(1)–B(2)–Mo(2) 78.7(3), Mo(1)–B(3)–Mo(2) 79.5(3), Mo(1)–B(4)–Mo(2) 78.2(3), Mo(1)–B(5)–Mo(2) 74.3(2).

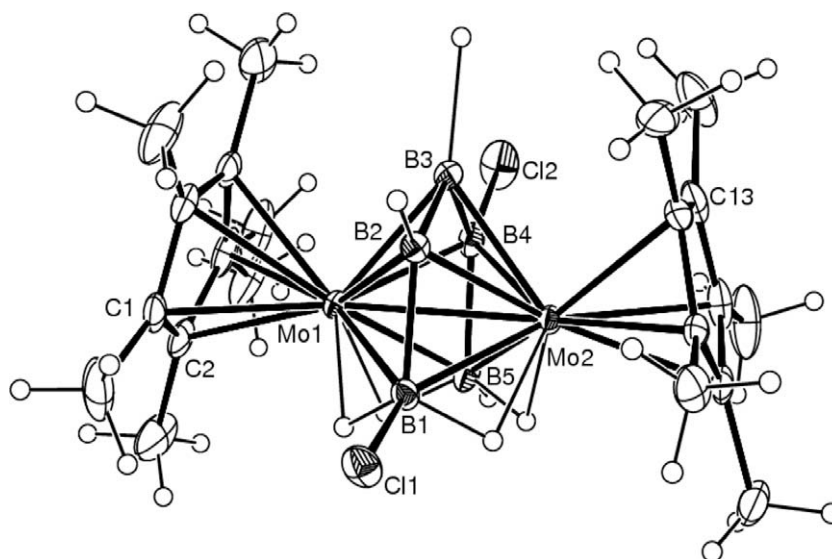


Fig. 2. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$ (**3**). Selected bond lengths (Å) and angles ($^\circ$): Mo(1)–Mo(2) 2.8276(4), Mo(1)–B(1) 2.315(4), Mo(1)–B(2) 2.227(4), Mo(1)–B(5), 2.328(4), Mo(2)–B(1) 2.320(4), Mo(2)–B(2) 2.224(4), Mo(2)–B(4) 2.28(4), Mo(2)–B(5) 2.335(4), B(1)–B(2) 1.751(5), B(2)–B(3) 1.709(5), B(3)–B(4) 1.720(6), B(4)–B(5) 1.755(6), B(4)–Cl(2) 1.814(4), B(1)–Cl(1) 1.830(4), Mo(1)–B(1)–Mo(2) 75.18(11), Mo(1)–B(2)–Mo(2) 78.88(12), Mo(1)–B(3)–Mo(2) 79.44(12), Mo(1)–B(5)–Mo(2) 74.66(12).

2.2. Synthesis and characterization of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Me}_m$ ($n = 6, 7; m = 3, 2$)

Reaction of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$, **1** with 5-fold excess of *n*-BuLi at -70°C followed by room temperature reaction with methyl iodide led to the isolation of two sets of B-Me inserted metallaboranes, $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7(\text{CH}_3)_2$ (**7**, **8** two isomers) and $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_6(\text{CH}_3)_3$ (**9**, **10** two isomers) (Scheme 1). Descriptions of the characterizations of the two sets of products, **7–10** from mass spectrometric, IR and multinuclear NMR spectroscopy follows.

The first set of products, **7** and **8** has been isolated in 30% yield as a mixture of two compounds roughly in a ratio of 60:40. The mass spectrum of the mixture showed a single parent ion envelope

suggesting the presence of two geometric isomers containing 2 methyl groups. Attempts to separate these isomers by TLC failed however, the ^{11}B and ^1H NMR signals of these isomers could be unambiguously assigned from the NMR spectrum of the mixture. The ^{11}B NMR spectrum shows two sets of boron resonances; one set contains three kinds of boron resonances in the ratio of 2:1:2 and the other set contains five kinds of boron resonances in the ratio of 1:1:1:1:1. The resonances at $\delta = 41.32$ ppm for **7**, and resonances at $\delta = 72.82$ and 38.65 ppm for **8**, have been assigned to borons associated with methyl group. Similarly, the ^1H NMR and ^{13}C NMR spectra show two sets of Cp $^+$ signals and both the sets contain only one kind of Cp $^+$ protons. Furthermore, the ^1H NMR spectrum of each set clearly shows the presence of B-H, methyl and Mo-H-B protons. No suitable crystals of **7** or **8** for structure

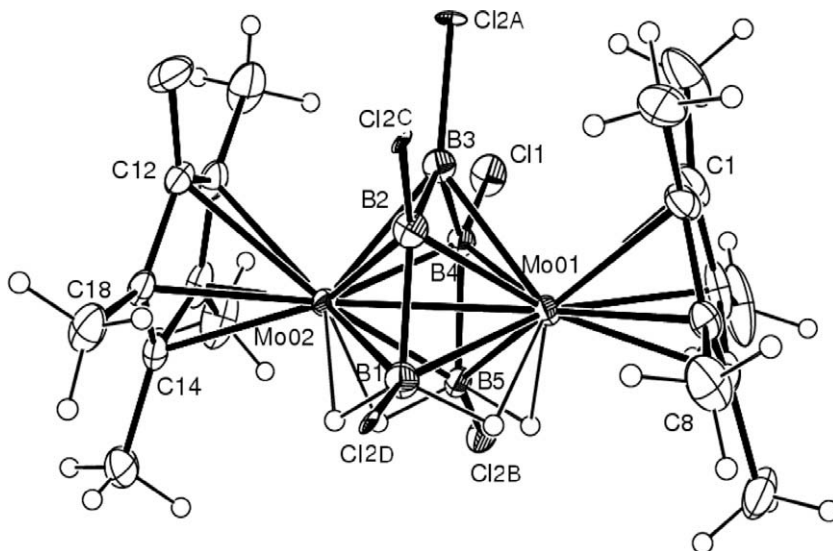


Fig. 3. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$ (**5**). The chlorine atom (Cl2) is disordered over four orientations (Cl2A, Cl2B, Cl2C and Cl2D) in the ratio of 0.12:0.79:0.04:0.03, respectively. Selected bond lengths (Å) and angles ($^\circ$): Mo(1)–Mo(2) 2.8262(5), Mo(1)–B(1) 2.346(5), Mo(1)–B(2) 2.233(5), Mo(1)–B(4) 2.212(5), Mo(1)–B(5), 2.314(5), Mo(2)–B(1) 2.344(5), Mo(2)–B(2) 2.236(5), Mo(2)–B(5) 2.313(5), B(1)–B(2) 1.738(8), B(2)–B(3) 1.710(7), B(4)–B(5) 1.777(7), B(1)–Cl(2D) 1.65(3), Mo(1)–B(1)–Mo(2) 74.10(16), Mo(1)–B(2)–Mo(2) 78.47(17), Mo(1)–B(3)–Mo(2) 79.71(18).

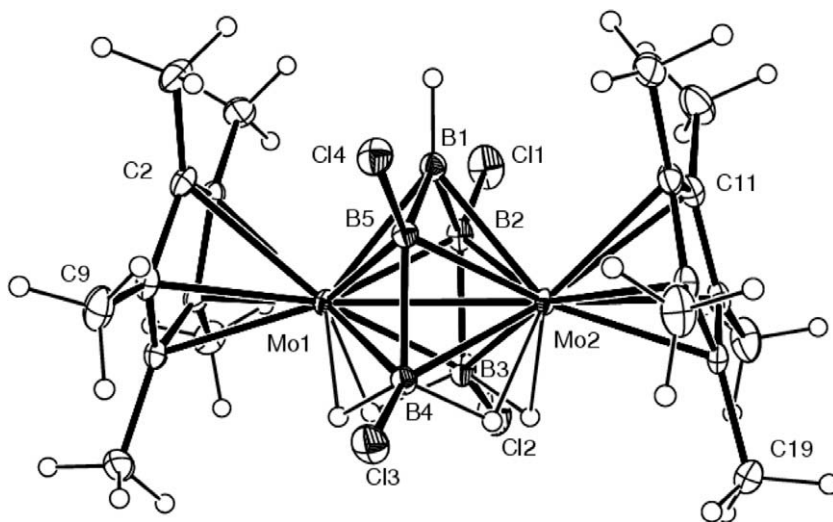


Fig. 4. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_5\text{Cl}_4$ (**6**). Selected bond lengths (Å) and angles ($^\circ$): Mo(1)–Mo(2) 2.8441(3), Mo(1)–B(1) 2.221(3), Mo(1)–B(2) 2.228(3), Mo(1)–B(4) 2.326(3), Mo(1)–B(5), 2.219(3), Mo(2)–B(1) 2.218(3), Mo(2)–B(2) 2.224(3), Mo(2)–B(4) 2.321(3), B(1)–B(2) 1.705(5), B(3)–B(4) 1.720(6), B(4)–B(5) 1.769(5), B(4)–Cl(3) 1.814(3), Mo(1)–B(1)–Mo(2) 79.69(12), Mo(1)–B(3)–Mo(2) 75.11(10), Mo(1)–B(4)–Mo(2) 75.46(10), Mo(1)–B(5)–Mo(2) 79.77(10).

determination were obtained but, comparing their spectroscopic data to those of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$ (**3–5**), their molecular formulas are best fit with the structures as shown in Scheme 1.

A second set of products, **9–10**, has been isolated in yields of 20% and 25% respectively as yellow solid. From the mass spectral analysis combined with the ^{11}B NMR spectra both **9** and **10** are formulated as $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_6\text{Me}_3$. The spectroscopic data show that compounds **9** and **10** are geometrical isomers differing only in the position of the Me and H groups relative to the Mo–Mo edge of the cluster. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **9** shows the substitution of three B–H protons by methyl groups and rationalizes the presence of four types of boron environment in the ratio of 1:2:1:1 and the resonance at 55.97 ppm of intensity two is an accidental overlap of two boron resonances. The ^1H NMR spectrum reveals two types of B–H protons in the ratio of 1:1, and the presence two kinds of Mo–H–B protons at $\delta = -6.94$ and -7.58 ppm respectively. Similarly, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **10** rationalized the

presence of five types of boron environment in the ratio of 1:1:1:1:1, where the resonances at $\delta = 54.93$, 39.47 and 22.40 ppm showed no coupling with hydrogen confirms the B–Me environments. All attempts to grow single crystals of **9** and **10** for X-ray structural study failed however, all the spectroscopic data are consistent with the proposed structure as shown in Scheme 1.

Molybdaborane, **1** can be lithiated with butyllithium, and treatment of the lithio species with methyl iodide led to the isolation of two sets of B-methylated products, disubstituted **7–8** and trisubstituted **9–10**. However, all of our attempts to synthesize permethylated $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5(\text{Me})_5\text{H}_4$ failed.

3. Conclusions

Exo-cluster substitution at B–H in molybdaborane cluster, $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$, **1** was achieved using $\text{BHCl}_2\text{-SMe}_2$ and MeI

reagents. As far as the primary synthetic objective these products increased the complexity of the problem. Several attempts of boron framework chlorination of **1** by $\text{BHCl}_2 \cdot \text{SMe}_2$ led decomposition and all efforts to substitute the fifth B-H in **6** directly with a chloride group using $\text{BHCl}_2 \cdot \text{SMe}_2$ were unsuccessful. Although we do not have any direct evidence of intermediates for the formation of **2–6** from **1**, these results seem to indicate that the formation of **1–6** occurs by direct incorporation of B-H or chloroborane B-Cl fragment(s) rather than H/Cl exchange.

4. Experimental

4.1. General procedures and instrumentation

All the operations were conducted under an Ar/N_2 atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under Argon. Cp^*H , $\text{Mo}(\text{CO})_6$, BuLi , $\text{BHCl}_2 \cdot \text{SMe}_2$, and LiBH_4 in THF purchased from Aldrich and used as received. Mel purchased from Aldrich and freshly distilled prior to use. $(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ was prepared with some modification of Green [49] work. The external reference for the ^{11}B NMR, $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ [50] and molybdaborane $\{(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9\}$, **1** [51] were 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 (MERK 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, benzene, 7.16), while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in C_6D_6 (δB , ppm, -30.07) was used as an external reference for the ^{11}B 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 mA) as the FAB gas.

4.2. Modified synthesis of Cp^*MoCl_4

A mixture of $[\eta^5\text{-C}_5\text{Me}_5]$ (0.323 g, 2.27 mmol) and $\text{Mo}(\text{CO})_6$ (0.5 g, 1.894 mmol) in 12 mL of THF was refluxed for 12 h. After 12 h of reflux it was stirred at room temperature for another 12 h which gave an orange yellow solution. To this yellow solution a five fold excess of freshly distilled Mel (0.6 mL, 9.47 mmol) was added and allowed to stir for 1 h, followed by 1 h reflux. The solvent was removed in vacuo and the yellow residue was extracted into pentane and filtration through Celite afforded yellow solid of $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{Me}$ (0.57 g, 92%). To a 6 mL CH_2Cl_2 solution of yellow $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{Me}$ (0.3 g, 0.91 mmol) a PCl_5 solution (0.47 g, 2.27 mmol, partially dissolved in 2 mL of CH_2Cl_2) was added and refluxed for 12 h. After 12 h reflux, the solvent was reduced to 2 mL. Removal of supernatant liquid and washing the solid two times with CH_2Cl_2 afforded pure purple microcrystalline Cp^*MoCl_4 (0.22 g, 64%).

4.3. Synthesis of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Cl}_m$ ($n = 5, 7$, and 8 ; $m = 4, 2$, and 1)

$(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ (0.5 g, 1.34 mmol) in 15 mL of toluene was treated with 6-fold excess of $\text{LiBH}_4 \cdot \text{thf}$ (4 mL, 8 mmol) at -40°C and allowed to stir at room temperature for 1 h. After removal of toluene residue was extracted into hexane and filtered through frit using Celite. The yellowish green hexane extract was dried under vacuo and taken in 20 mL of toluene and thermolysed at 90°C with 6-fold excess of $\text{BHCl}_2 \cdot \text{SMe}_2$ (0.92 mL, 8 mmol) for 20 h. The solvent was evaporated in vacuo, residue was extracted into hexane and passed through Celite mixed with 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: CH_2Cl_2 (90:10 v/v) yielded six bands. They are $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$, **1** (0.15 g, 22%), $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_8\text{Cl}$, **2** (0.11 g, 15%), red $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **3** (0.08 g, 10%), orange yellow $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **4** (0.05 g, 6%), yellow $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **5** (0.06 g, 8%), and light yellow $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_5\text{Cl}_4$, **6** (0.03 g, 4%).

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_8\text{Cl}$, **2**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 560 (isotopic pattern for 2Mo, 1Cl and 5B atoms); ^{11}B NMR (CDCl_3 , 22°C): δ 65.77 (d, 1B-H), 57.79 (br, 2B-H), 37.91 (s, 1B-Cl), 22.67 (d, 1B-H); ^1H NMR (CDCl_3 , 22°C): δ 5.76 (s, 1BHt), 4.57 (s, 1BHt), 4.44 (s, 2BHt), 2.03 (s, 30H, Cp^*), -5.93 (d, 2Mo-H-B), -6.84 (d, 2Mo-H-B); IR (hexane, cm^{-1}): 2455w, 2471w (B-Ht); elemental analysis calcd (%) for $^{12}\text{C}_{20}^{1}\text{H}_{38}^{11}\text{B}_5^{35}\text{Cl}^{96}\text{Mo}_2$: C 42.90, H 6.84; found: C 41.41, H 6.56.

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **3**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 594 (isotopic pattern for 2Mo, 2Cl and 5B atoms); ^{11}B NMR (CDCl_3 , 22°C): δ 68.63 (s, 1B-Cl), 62.68 (br, 1B-H), 59.55 (br, 1B-H), 38.57 (s, 1B-Cl), 26.2 (d, 1B-H); ^1H NMR (CDCl_3 , 22°C): δ 5.64 (s, 1BHt), 4.89 (s, 1BHt), 3.38 (s, 1BHt), 2.08 (s, 30H, Cp^*), -5.36 (d, 2Mo-H-B), -6.19 (d, 2Mo-H-B); IR (hexane, cm^{-1}): 2471w (B-Ht); elemental analysis calcd (%) for $^{12}\text{C}_{20}^{1}\text{H}_{37}^{11}\text{B}_5^{35}\text{Cl}_2^{96}\text{Mo}_2$: C 40.42, H 6.27; found: C 41.32, H 6.67.

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **4**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 594 (isotopic pattern for 2Mo, 2Cl and 5B atoms); ^{11}B NMR (CDCl_3 , 22°C): δ 70.36 (s, 2B-Cl), 60.4 (br, 1B-H), 21.75 (d, 2B-H); ^1H NMR (CDCl_3 , 22°C): δ 5.43 (pcq, 1BHt), 4.66 (pcq, 1BHt), 4.13 (pcq, 1BHt), 2.10 (s, 30H, Cp^*), -6.41 (br, 4 Mo-H-B); IR (hexane, cm^{-1}): 2455w, 2471w (B-Ht); elemental analysis calcd (%) for $^{12}\text{C}_{20}^{1}\text{H}_{37}^{11}\text{B}_5^{35}\text{Cl}_2^{96}\text{Mo}_2$: C 40.42, H 6.27; found: C 41.82, H 6.86.

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7\text{Cl}_2$, **5**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 594 (isotopic pattern for 2Mo, 2Cl and 5B atoms); ^{11}B NMR (CDCl_3 , 22°C): δ 72.38 (s, 1B-Cl), 58.26 (br, 1B-H), 56.66 (s, 1B-Cl), 36.76 (br, 1B-H), 22.54 (br, 1B-H); ^1H NMR (CDCl_3 , 22°C): δ 4.7 (pcq, 1BHt), 4.40 (pcq, 1BHt), 3.43 (pcq, 1BHt), 2.03 (s, 30H, Cp^*), -5.51 (d, 2Mo-H-B), -6.53 (d, 2Mo-H-B); IR (hexane, cm^{-1}): 2451w, 2503w (B-Ht); elemental analysis calcd (%) for $^{12}\text{C}_{20}^{1}\text{H}_{37}^{11}\text{B}_5^{35}\text{Cl}_2^{96}\text{Mo}_2$: C 40.42, H 6.27; found: C 39.20, H 6.11.

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_5\text{Cl}_4$, **6**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 664 (isotopic pattern for 2Mo, 4Cl and 5B atoms); ^{11}B NMR (CDCl_3 , 22°C): δ 66.03 (s, 2B-Cl), 54.98 (br, 1B-H), 36.61 (s, 2B-Cl); ^1H NMR (CDCl_3 , 22°C): δ 6.99 (s, 1BHt), 1.76 (s, 30H, Cp^*), -5.08 (br, 4Mo-H-B); IR (hexane, cm^{-1}): 2448w (B-Ht); elemental analysis calcd (%) for $^{12}\text{C}_{20}^{1}\text{H}_{35}^{11}\text{B}_5^{35}\text{Cl}_4^{96}\text{Mo}_2$: C 36.22, H 5.32; found: C 35.01, H 4.98.

4.4. Synthesis of $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Me}_m$ ($n = 6, 7$; $m = 3, 2$)

In a flame-dried schlenk tube, $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$, **1** (0.1 g, 0.19 mmol) was dissolved in 5 mL of THF and cooled to -70°C . To this cold yellow solution, BuLi (0.6 mL, 0.95 mmol) was added via syringe and the reaction mixture was warmed slowly over 30 min to room temperature and left stirring for 20 minutes. To this purple solution, Mel (0.12 mL, 1.9 mmol) was added and allowed to stir at room temperature for 4 h. The solvent was dried under vacuo 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 hexane/ CH_2Cl_2 mixture (97:3 v/v) yielded yellow $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7(\text{CH}_3)_2$, **7** and $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7(\text{CH}_3)_2$, **8** (0.03 g, 30% yield as a mixture of two compounds), orange $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_6(\text{CH}_3)_3$, **9** (0.02 g, 20%) and orange $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_6(\text{CH}_3)_3$, **10** (0.02 g, 25%).

$(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_7(\text{CH}_3)_2$, **7 and 8 mixture**: MS (FAB) $\text{P}^+(\text{max})$: m/z (%) 554 (isotopic pattern for 2Mo, 5B atoms and two Me groups); ^{11}B NMR (CDCl_3 , 22°C): δ 60.70 (d, 2B-H), 51.84 (d, 1B-H) and 41.32 (s, 2B-Me) for **7**; δ 72.82 (s, B-Me), 63.53 (d, 1B-H), 51.69 (d, B-H), 38.65 (s, B-Me) and 23.59 (br, B-H) for **8**; ^1H NMR

Table 1
Crystallographic data for compounds **2**, **3**, **5** and **6**.

	2	3	5	6
Formula	C ₂₀ H ₃₈ B ₅ ClMo ₂	C ₂₀ H ₃₇ B ₅ Cl ₂ Mo ₂	C ₂₀ H ₃₇ B ₅ Cl ₂ Mo ₂	C ₂₀ H ₃₅ B ₅ Cl ₄ Mo ₂
Formula weight	559.88	594.33	594.33	663.21
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P $\bar{1}$	P $\bar{1}$	P 2 ₁ /c	Pbca
a (Å)	8.8298(4)	8.8461(2)	14.2703(9)	17.0117(4)
b (Å)	9.5333(4)	9.6028(2)	14.4663(6)	14.7262(3)
c (Å)	15.0993(6)	15.2334(3)	12.5873(6)	20.9664(4)
α (°)	99.587(2)	99.1640(10)	90.00	90.00
β (°)	96.577(2)	97.6110(10)	103.986(2)	90.00
γ (°)	99.305(2)	99.3540(10)	90.00	90.00
V (Å ³)	1223.63(9)	1243.77(5)	2521.5(2)	5252.45(19)
Z	2	2	4	8
D _{calcd} (g/cm ³)	1.520	1.587	1.558	1.677
F(000)	568	600	1188	2656
μ (mm ⁻¹)	1.138	1.229	1.212	1.370
Crystal size (mm)	0.20 × 0.20 × 0.10	0.40 × 0.20 × 0.20	0.22 × 0.20 × 0.15	0.22 × 0.21 × 0.19
θ range (°)	1.38–28.43	1.37–28.30	1.47–28.32	2.28–28.29
Goodness-of-fit (GOF)	1.249	1.187	1.121	1.136
R indices	R ₁ = 0.0552	R ₁ = 0.0358	R ₁ = 0.0462	R ₁ = 0.0316
[I > 2 σ (I)]	wR ₂ = 0.1598	wR ₂ = 0.0906	wR ₂ = 0.1189	wR ₂ = 0.0811
R indices	R ₁ = 0.0735	R ₁ = 0.0412	R ₁ = 0.0556	R ₁ = 0.0383
[I > 2 σ (I)]	wR ₂ = 0.1861	wR ₂ = 0.0972	wR ₂ = 0.1279	wR ₂ = 0.0856
Largest difference in peak and hole (e/Å ³)	1.719 and –1.077	3.786 and –1.096	4.300 and –0.765	3.231 and –0.782

(CDCl₃, 22 °C): δ 4.87 (br, 2Bht), 2.44 (br, 1Bht), 1.98 (s, 30H, Cp^{*}), 0.90 (m, 6H, 2Me), –7.31 (br, 4Mo-H-B) for **7**; δ 5.30 (br, 2Bht), 4.84 (s, 1Bht), 2.02 (s, 30H, Cp^{*}), 1.11 (m, 3H, 1Me), 0.90 (m, 3H, 1Me), –7.92 (d, 2Mo-H-B), and –8.21 (d, 2Mo-H-B) for **8**; ¹³C NMR (CDCl₃, 22 °C): δ 105.3 (C₅Me₅), 11.7 (C₅Me₅) and 0.36 (B-CH₃) for **7**; δ 106.6 (C₅Me₅), 12.7 (C₅Me₅) and 1.01 (B-Me) for **8**; IR (CDCl₃, cm⁻¹): 2490w, 2454w (B-Ht).

(η^5 -C₅Me₅Mo)₂B₅H₆(CH₃)₃, **9**: MS (FAB) P⁺(max): *m/z* (%) 568 (isotopic pattern for 2Mo, 5B atoms and three Me groups); ¹¹B NMR (CDCl₃, 22 °C): δ 66.59 (d, 1B-H), 55.97 (s, 2B-Me), 41.73 (s, B-Me), 22.83 (br, B-H); ¹H NMR (CDCl₃, 22 °C): δ 4.55 (br, 1Bht), 4.32 (br, 1Bht), 2.07 (s, 30H, Cp^{*}), 1.34 (m, 3H, 1Me), 1.27 (m, 3H, 1Me), 0.91 (m, 3H, 1Me), –6.94 (br, 2Mo-H-B), –7.58 (br, 2Mo-H-B); ¹³C NMR (CDCl₃, 22 °C): δ 105.9 (C₅Me₅), 11.79 (C₅Me₅), 0.75 (B-Me); IR (CDCl₃, cm⁻¹): 2492w, 2454 w (B-Ht).

(η^5 -C₅Me₅Mo)₂B₅H₆(CH₃)₃, **10**: MS (FAB) P⁺(max): *m/z* (%) 568 (isotopic pattern for 2Mo, 5B atoms and three Me groups); ¹¹B NMR (CDCl₃, 22 °C): δ 68.25 (d, 1B-H), 56.94 (d, 1B-H), 54.93 (s, 1B-Me), 39.47 (s, 1B-Me), 22.40 (s, 1B-Me); ¹H NMR (CDCl₃, 22 °C): δ 4.95 (br, Bht), 4.48 (br, 1Bht), 2.01 (s, 30H, Cp^{*}), 1.31 (m, 3H, 1Me), 1.26 (m, 3H, 1Me), 0.88 (m, 3H, 1Me), –6.97 (br, 2Mo-H-B), –7.29 (br, 2Mo-H-B); ¹³C NMR (CDCl₃, 22 °C): δ 105.7 (C₅Me₅), 11.10 (C₅Me₅), –0.73 (B-Me); IR (CDCl₃, cm⁻¹): 2494w, 2456w (B-Ht); elemental analysis calcd (%) for ¹²C₂₃¹H₄₅¹¹B₅⁹⁶Mo₂: C 48.67, H 7.99; found: C 49.94, H 8.21.

4.5. X-ray structure determinations

Crystal data were collected and integrated using Bruker Apex II CCD area detector system equipped with graphite monochromated Mo-K α (λ = 0.71073 Å) radiation at 173 K. The structure was solved by heavy atom methods using SHELXS-97 and refined using SHELXL-97 (Sheldrick, G.M., University of Göttingen). X-ray quality crystals were grown by slow diffusion of a hexane: CH₂Cl₂ (9.5:0.5 v/v) solution of **2**, **3**, **5** and **6**. Crystallographic information for compounds **2**, **3**, **5** and **6** are given in Table 1.

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Appendix A. Supplementary data

CCDC 695655, 695657, 695654 and 695656 contain the supplementary crystallographic data for **2**, **3**, **5**, and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the on-line version, at doi:10.1016/j.jorganchem.2008.10.036.

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