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Chemistry of Molybdaboranes: Synthesis, Structures, and Characterization of a New Class of Open-Cage Dimolybdaheteroborane Clusters

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Reaction of [Cp*MoCl$_4$], **1** (Cp* = η^5-C$_5$Me$_5$), with [LiBH$_4$·thf] in toluene at −70 °C, followed by pyrolysis with excess dichalcogenides RE-ER (R = Ph, CH$_2$Ph, 2,6-(^{t}Bu)$_2$-C$_6$H$_2$OH, (CH$_3$)$_3$C = ^{t}Bu); E = S, Se) yielded a new class of hybrid clusters, **3**−**8**: (**3**, [(Cp*Mo)$_2$(μ-η^1-SPh)$_2$(μ_3-S)(H$_2$BSPh)]; **4**, [(Cp*Mo)$_2$B$_5$H$_8$(SPh)]; **5**, [(Cp*Mo)$_2$B$_5$H$_8$(SePh)]; **6**, [(Cp*Mo)$_2$B$_2$S$_2$H$_2$(μ-η^1-S)]; **7**, [(Cp*Mo)$_2$B$_2$H$_5$(BSR)$_2$(μ-η^1-SR)], (R = 2,6-(^{t}Bu)$_2$-C$_6$H$_2$OH); and **8**, [(Cp*Mo)$_2$B$_2$H$_5$(BSePh)$_2$(μ-η^1-SePh)]. Compounds **3**−**8** have been isolated in modest yields as green or brown crystalline solids. In parallel with **3**−**8**, [(Cp*Mo)$_2$B$_5$H$_9$] was isolated as a major product in all cases. The isolation and structural characterization of compounds **3** and **6**−**8** provided the first direct evidence of the existence of [(Cp*Mo)$_2$B$_4$H$_8$], **2**, an intermediate in the formation of [(Cp*Mo)$_2$B$_5$H$_9$]. These new compounds have been characterized in solution by mass spectrometry, ^{1}H, ^{11}B, ^{13}C NMR, and IR spectroscopy, and elemental analysis. The structural types were unequivocally established by X-ray crystallographic analysis of compounds **3**−**8**.

Introduction

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.[1−3] Metallaheteroborane compounds containing group 16 elements as cluster constituents[4,5] have mostly been generated from the reaction of metal centers with preformed polyhedral heteroborane substrates.[6,7] However, after it had been

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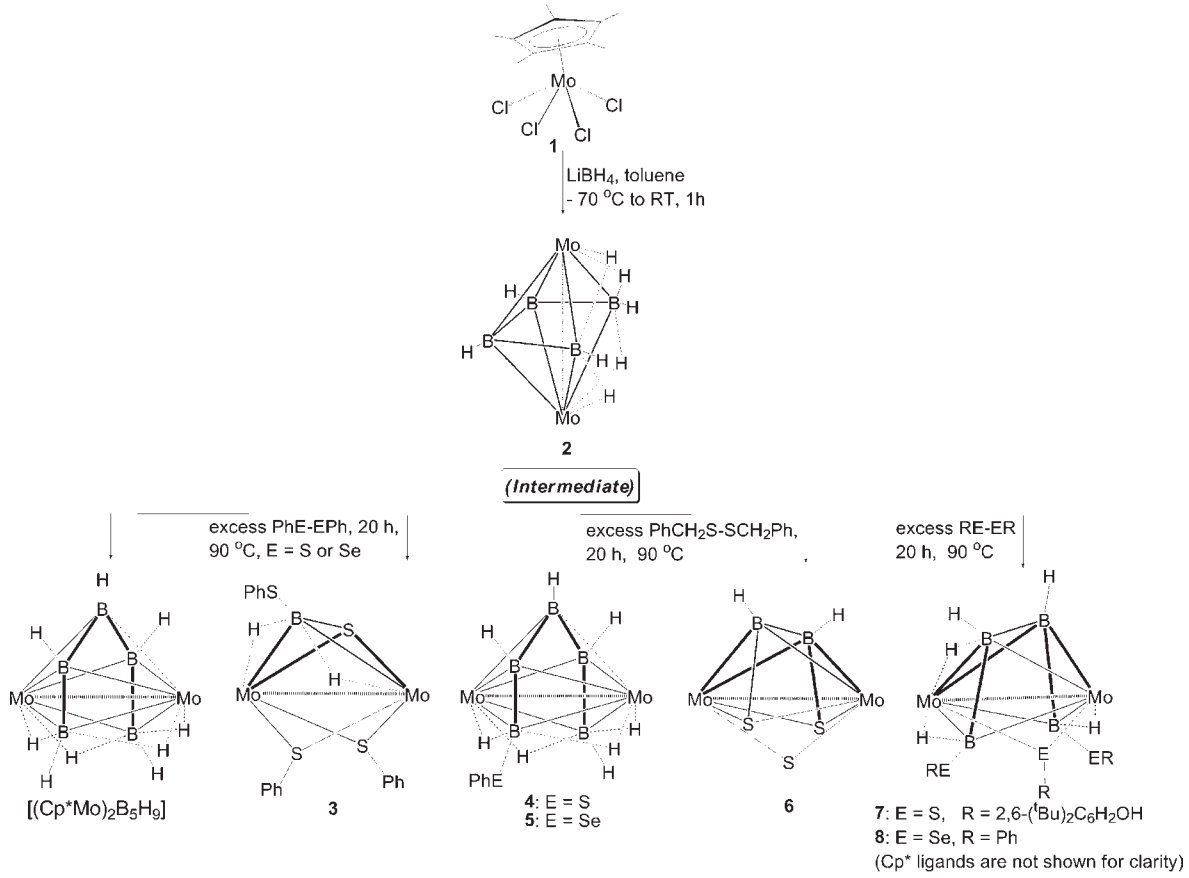
Scheme 1



discovered that the reaction of [Cp*$MoCl_4$] with [BH_3·thf] led to the isolation of two eight-vertex oxamolybdaborane clusters, [$(Cp^*Mo)_2B_5(\mu_3\text{-OEt})H_6R$] (R = H and *n*-BuO),[8] an investigation of metallaheteroboranes containing group 16 elements, other than oxygen, became of interest. As dimolybdaheteroboranes are rare, and structurally characterized examples even more so, we have begun to investigate the use of different chalcogen sources which might result in the generation of new types of cluster systems. In this paper, we present a set of open-cage dimolybdaheteroborane compounds obtained from the pyrolysis of dichalcogenides and an in situ generated intermediate, produced from the reaction between **1** and [$LiBH_4$·thf].

Results and Discussion

Although compounds **3**−**8** are produced in a mixture along with [$(Cp^*Mo)_2B_5H_9$][9] (Scheme 1), these compounds can be separated by preparative thin layer chromatography (TLC) which allowed spectroscopic and structural characterization of pure materials. These reactions utilized dichalcogenide reagents as a chalcogen source, and it is noteworthy that in half of the cases the dimetallaheteroborane compounds retain the same number of boron framework atoms. Further, the difference in reactivity between the dichalcogenide reagents is also reflected in the isolation of edge-fused cluster **3** in the PhS-SPh case, in contrast to the clean synthesis of **7** and **8** by the use of [$(2,6\text{-}(^t\text{Bu})_2\text{-}C_6H_2OH)_2S_2$] and [PhSe-SePh], respectively. Descriptions of the characterizations of **3**−**8** from mass spectrometric, NMR, and X-ray diffraction studies follow.

[$(Cp^*Mo)_2(\mu\text{-}\eta^1\text{-SPh})_2(\mu_3\text{-S})(H_2BSPh)$], 3. Mass spectral data of **3** suggest a molecular formula of $C_{38}H_{47}BS_4Mo_2$, and the ^{11}B NMR spectrum indicates the presence of a single resonances at $\delta = -17.7$ ppm. The ^{11}B chemical shift is consistent with hydrogen-bridged rather than direct Mo−B linkages. The ^{1}H NMR spectrum reveals a single Cp* resonance (relative intensity 30) and one Mo−H−B resonance at $\delta = -11.50$ ppm (intensity 2). The ^{13}C NMR spectrum also reveals the presence of one set of Cp* resonances. The IR spectrum of **3** shows a band at 459 cm^{-1} in a region characteristic of the Mo−S stretching frequency. Single crystal X-ray diffraction structure of **3**, shown in Figure 1, confirms the structural inferences made on the basis of spectroscopic results.

Compound **3** may be described as an edge-fused molybdathiaborane cluster, giving each Mo center a formal oxidation state of (IV). The molecular structure shows two Cp*Mo units linked by a pair of bridging SPh ligands and in a side-on fashion by a $SPhH_2BS$ unit. The interesting feature of the structure is the nearly square planar arrangement of one boron and three sulfur atoms, perpendicular to the Mo1−Mo2 bond and parallel to the two Cp* planes. Two types of sulfur ligands are found: (i) μ_2-S, (S2 and S3) and (ii) μ_3-S (S4). The μ_3-S ligand is connected to the boron atom and the observed B(1)−S(4) bond length of 1.852(5) Å is comparable to that of other sulfur-containing metallathiaborane compounds.[6] On the other hand, the μ_2-S ligands, bridged between two molybdenum centers, are symmetric with an average metal−sulfur

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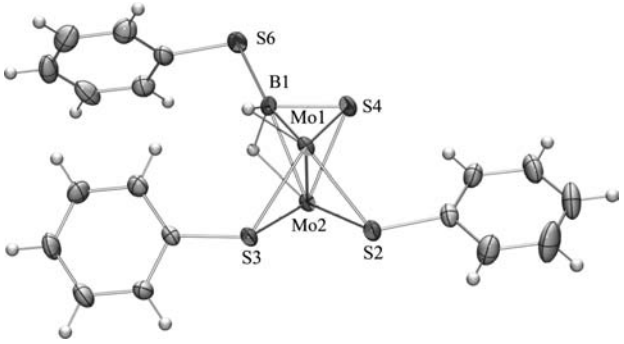

Figure 1. Molecular structure of $[(Cp^*Mo)_2(\mu_3\text{-}S)(\mu\text{-}\eta^1\text{-}SPh)_2(H_2BSPh)]$, **3** (Cp* ligands are not shown for clarity). Selected interatomic distances (Å) and angles (deg): Mo(1)−Mo(2) 2.6962(5), Mo(2)−B(1) 2.443(5), Mo(1)−B(1) 2.428(4), Mo(2)−S(4) 2.4539(11), Mo(1)−S(4) 2.4424(10), Mo(1)−S(3) 2.4496(10), Mo(2)−S(3) 2.4635(10), Mo(2)−S(2) 2.4492(11), Mo(1)−S(2) 2.4727(12), S(6)−B(1) 1.874(5), S(4)−B(1) 1.852(5); Mo(1)−S(4)−B(1) 67.23(14), Mo(1)−S(3)−Mo(2) 66.57(3), S(3)−Mo(2)−S(4) 112.02(4).

bond length of 2.458 Å and an Mo−S−Mo angle of 66.5°, which is comparable to the symmetric coordination of the disulfide bridges in $[(Cp^*\ Mo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$. The Mo−S bond lengths of S(2), S(3), and S(4) are slightly longer than those in related Mo (IV) complexes.[10] Bridging of the dimetal unit by B(1) and S(4) is analogous to the interaction of the $B_2H_6^{2-}$ ligand with a dinuclear group 5 unit in $[(C_5Me_5M)_2(B_2H_6)_2]$ (M = V, Nb, or Ta), [(*p*-tol)NCH-N(*p*-tol)$_4$$Ta_2B_2H_6$], and $[(C_5Me_5TaBr)_2B_2H_6]$.[11−16] Similarities in the Mo−Mo bond length (2.696(5) Å) and Mo(μ-SPh)Mo angles (66.57, 66.43°) of the Mo(μ-SPh)$_2$-Mo unit with those reported for $[(C_5H_4{}^iPr)Mo(\mu\text{-}Cl)_2]_2$ (2.607(1) Å and 63.17, 63.34°, respectively)[17] are consistent with a single bond connecting two Mo(IV) centers.

$[(Cp^*Mo)_2B_5H_8(EPh)]$, (4: E = S; 5: E = Se). Compounds **4** and **5** have been isolated following preparative TLC in yields of 9 and 7%, respectively, and characterized by comparison of their spectroscopic data with other similar B−H substituted compounds.[18] The mass spectrometry measurements of **4** and **5** gave molecular ions corresponding to $C_{26}H_{43}B_5SMo_2$ and $C_{26}H_{43}B_5SeMo_2$, respectively. The ^{11}B NMR spectrum of **5** indicates the presence of five boron environments in a ratio of 1:1:1:1:1. The resonances at δ = 34.2 and 30.3 ppm for **4** and **5**, respectively, showed no coupling, thus confirming the B-SPh and B-SePh environments. Furthermore, the $^1H\{^{11}B\}$ NMR spectra of **4** and **5** showed one type of Cp* protons, four types of B−H protons, and two types of Mo−H−B protons.

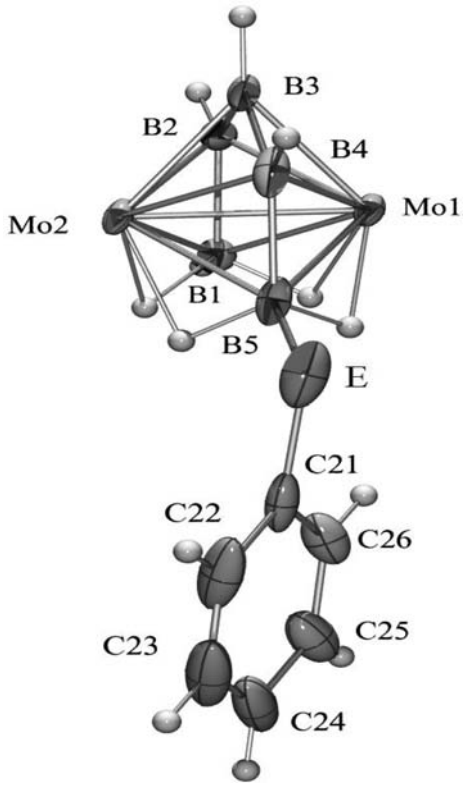

Figure 2. Molecular structure of compounds **4** and **5**. (Cp* ligands are not shown for clarity). Selected interatomic distances (Å) and angles (deg): **4**: Mo(1)−Mo(2) 2.8106(10), Mo(1)−B(1) 2.324(4), Mo(1)−B(2) 2.225(4), Mo(1)−B(3) 2.196(4), Mo(1)−B(4) 2.218(4), Mo(1)−B(5), 2.318(4), Mo(2)−B(1) 2.322(4), Mo(2)−B(2) 2.217(5), Mo(2)−B(3) 2.182(4), Mo(2)−B(4) 2.213(4), Mo(2)−B(5) 2.324(4), B(1)−B(2) 1.747(5), B(2)−B(3) 1.715(6), B(3)−B(4) 1.711(8), B(5)−S(1) 1.887(4); B(2)−B(1)−Mo(1) 64.45(17). **5**: Mo(1)−Mo(2) 2.8165(3), Mo(1)−B(1) 2.326(3), Mo(1)−B(2) 2.220(3), Mo(1)−B(3) 2.197(3), Mo(1)−B(4) 2.218(3), Mo(1)−B(5), 2.314(3), Mo(2)−B(1) 2.330(3), Mo(2)−B(2) 2.219(3), Mo(2)−B(3) 2.196(3), Mo(2)−B(5) 2.316(3), B(1)−B(2) 1.753(4), B(4)−B(5) 1.739(5), B(5)−Se(1) 2.025(3); B(4)−B(3)−B(2) 121.3(2).

Single crystals suitable for X-ray diffraction analysis of **4** and **5** were obtained from a hexane solution at −4 °C, thus allowing structural characterization and confirmation of the structural inferences made on the basis of spectroscopic results. The solid state structure of **4** and **5**, shown in Figure 2, is similar to that of $[(Cp^*M)_2B_5H_9]$, (M = Cr, Mo, W)[9,19] and $[(Cp^*ReH)_2B_5Cl_5]$,[20] and is best described as a bicapped *closo* trigonal bipyramid. The observed Se−B bond length of 2.025(4) Å in **5** is significantly longer than those observed in $[NEt_4]_2[Se_3B_{11}H_9]$, a disubstituted derivative of $[closo\text{-}B_{11}H_{11}]^{2-}$.[21]

Existence of compounds **4** and **5** permits a structural comparison with $[(Cp^*Mo)_2B_5H_9]$ and its derivatives,[9,18,22] and the important geometrical parameters and ^{11}B chemical

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Table 1. Selected Structural Parameters and ^{11}B Chemical Shifts of **4**, **5**, and Related Species

compounds	d[M−M] [Å]	avg.[Mo−B][a] [Å]	dihedral angle [deg][b]	^{11}B NMR (ppm)
$(Cp^*Mo)_2B_5H_9$[9]	2.80	2.31	121.5	62.9, 25.8
$(Cp^*Mo)_2B_5H_8(n\text{-Bu})$[22]	2.79	2.33	122.9	66.4, 57.2, 55.8, 41.5, 22.6
$(Cp^*Mo)_2B_5H_8Cl$[18a]	2.81	2.30	122.3	65.7, 57.8, 37.9, 22.6
$(Cp^*W)_2B_5H_8Cl$[18b]	2.82	2.29	122.7	50.6, 45.1, 44.1, 42.6, 24.3
4	2.81	2.32	121.8	62.1, 61.5, 34.2, 24.2
5	2.81	2.31	121.9	64.1, 62.4, 59.8, 30.7, 24.7

[a] The average Mo−B distance found in cage. [b] Dihedral angles of the hydrogen bridged butterfly face.

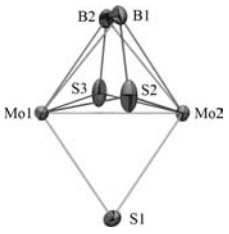

Figure 3. Molecular structure of $[(Cp^*Mo)_2B_2S_2H_2(\mu\text{-}\eta^1\text{-S})]$, **6** ($Cp^*$ ligands are not shown for clarity). Selected interatomic distances (Å) and angles (deg): Mo(1)−Mo(2) 2.6359(16), Mo(1)−B(1) 2.372(12), Mo(2)−B(1) 2.341(13), Mo(2)−S(2) 2.389(3), B(1)−B(2) 1.69(4), B(1)−S(2) 1.829(19); Mo(1)−S(1)−Mo(2) 68.11(13), Mo(1)−S(2)−Mo(2) 67.07(9), Mo(1)−S(2)−B(1) 67.1(4), Mo(2)−S(2)−B(1) 68.7(5).

shifts are listed in Table 1. Although the Mo1−Mo2 bond lengths in **4** and **5** are longer than those observed in $[(Cp^*Mo)_2B_5H_9]$, the dihedral angles of the hydrogen-bridged butterfly face are similar. The observed discrepancies in structural parameters and ^{11}B chemical shifts may be due to the perturbation of the electronic environment of the boron atoms by ligands.

$[(Cp^*Mo)_2B_2S_2H_2(\mu\text{-}\eta^1\text{-S})]$, 6. Compound **6** was isolated as a green, relatively air-stable solid. The mass spectrometric data suggest a molecular formula of $C_{20}H_{32}Mo_2B_2S_3$ and the ^{11}B NMR data (single resonance at $\delta = 18.8$ ppm) suggests a structure, if static, of higher symmetry. Consistent with this observation, **6** indeed shows one kind of Cp* signal. Molecular structure of **6**, shown in Figure 3, reveals that there are two independent molecules cocrystallized in a 1:1 ratio, one is the known $[(Cp^*Mo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$,[10] and the other is **6**. It is a notable example of organomolybdenum chalcogenide clusters in which the $[Mo_2B_2S_2]$ atoms define a bicapped tetrahedral framework, with one $\mu\text{-}\eta^1$-S ligand bridged between two molybdenum centers.

A similar structural interpretation has also been suggested by Sneddon for $[(CpCo)_2B_2S_2H_2]$ ($Cp = C_5H_5$).[6a,b] The cage has C_{2v} symmetry with the Mo atoms located in the apical positions and the boron and sulfur atoms in equatorial positions of the parent pentagonal bipyramidal polyhedron. In the molecular structure of **6** the two Mo atoms and the two sulfur atoms are situated on the open face of the cluster and allow two sulfur atoms to adopt lower coordinate positions in the polyhedron. Concomitantly a contraction of the metal−metal bond to 2.6359(16) Å was observed. This short distance is within the range typical for Mo═Mo bonds, as in binuclear alkoxy-bridge Mo(IV) complexes,[10] and comparable to that of oxamolybdaboranes.[8] The metal−metal interaction seems to be affected by the formal oxidation state of metal, as well as by the nature of the sulfur bridges. Although the avg. B−B and B−S distances in **6** are comparable to those of $[(CpCo)_2B_2S_2H_2]$ and other analogous systems[23] (Table 2), the metal−metal distances in **3** and **6**−**8** are much shorter in comparison with those of their nonchalcogenide analogues.[24−26]

$[(Cp^*Mo)_2B_2H_5(BER)_2(\mu\text{-}\eta^1\text{-ER})$, (7: E = S, R = 2,6-(^{t}Bu)$_2$-C_6H_2OH), 8: E = Se, R = Ph). In contrast to the results obtained using diphenyldisulfide, pyrolysis with (2,6-(^{t}Bu)$_2$-$C_6H_2OH)_2S_2$ and PhSe-SePh generated **7** and **8**, respectively. The molecular structures of **7** and **8**, shown in Figure 4, clearly show that both the compounds retain the same number of boron atoms as the intermediate during the course of reaction with dichalcogenides. These clusters are closely related to **6**, in that the μ_2-S and μ_3-S ligands are replaced by −E(R) and −B(HER) respectively, resulting in the same number of cluster framework electrons. The occurrence of two more bridged sulfur atoms would be expected to contract the Mo−Mo bond in **6**. Indeed, the Mo−Mo bond length of 2.6375(12) Å in **6**, is about 0.07 Å shorter than the Mo−Mo bond in **7** or **8**. In **6**, the Mo−Mo bond is bridged by three sulfido ligands, whereas there is only one such bridge in **7** and **8**. Compounds **6**, **7**, and **8** can be described as $(Cp^*Mo)_2(BH)_2$ dimetallatetrahedranes capped on each Mo_2B face with a μ_3-S group in **6** and −B(HER) group in **7** and **8**.

Consistent with the X-ray results, the ^{11}B NMR spectra of both **7** and **8** rationalize the presence of four boron resonances in a ratio of 1:1:2. The resonances appearing in the high field regions showed no coupling in the ^{11}B NMR spectrum confirming the B-SePh or B−S(2,6-(^{t}Bu)$_2$-C_6H_2OH) environments. The $^1H\{^{11}B\}$ NMR spectrum of compound **8** reveals two types of B−H protons and two kinds of Mo−H−B protons each at $\delta = -6.58$ and −8.58 ppm with intensity ratio 2:1. Furthermore, ^{1}H and ^{13}C NMR spectra of compound **7** and **8** confirmed the presence of two kinds of Cp* ligands in a 1:1 ratio. The Cp* ligands in both **7** and **8** are asymmetrically bonded to the molybdenum centers and are tilted from the mean plane of the four boron and one sulfur atom such that the dihedral angles between them are 7.9°, 8.7° for **7** and 9.1°, 12.8° for **8**. The $^1H\{^{11}B\}$-$^{11}B\{^1H\}$ HETCOR and variable temperature $^1H\{^{11}B\}$ NMR also support the structures of **7** and **8** as shown in Scheme 1. At room temperature the $^1H\{^{11}B\}$ NMR of compound **8** shows two resonances at $\delta = -6.58$ and $\delta = -8.58$ ppm. As the temperature is

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Table 2. Selected Structural Parameters and Dihedral Angles of **3**, **6**−**8**, and Other Related Compounds

compound	sep[a]	*d*[M−M] [Å]	avg. *d*[M−B] [Å]	*d*[B−B][b] [Å]	dihedral angle [deg][c]	^{11}B NMR [ppm]
$[(Cp^*Cr)_2B_4H_8]$[24]	5	2.87	2.06	3.02	147.6	34.3, 126.5
$[(Cp^*ReH_2)_2B_4H_4]$[25]	6	2.81	2.17	3.20	163.4	1.30, 68.7
$[(Cp^*Ta)_2B_4H_{10}]$[26]	5	2.89	2.38	3.68	167.7	0.3, 16.6
$[(CpCo)_2\ B_2S_2H_2]$	8	3.06	2.16	3.11[d]		17.6
3	6	2.69	2.43	2.79[e]	94.3[f]	−17.7
6	6	2.63	2.48	3.93[g]	161.9	18.8
7	6	2.69	2.29	3.72	164.2	84.4, 49.8, 30.45
8	6	2.70	2.27	3.69	168.0	78.8, 54.0, 19.2

[a] sep = skeletal electron pair. [b] Distance between two capped boron atoms (B_1 and B_4) in the open face of bicapped tetrahedral geometry. [c] Dihedral angle of M_2B_2 tetrahedral geometry. [d] Distance between two capped sulfur atoms (S_2 and S_3) in the open face. [e] Distance between S_2 and S_3. [f] Dihedral angle between $Mo_1S_2Mo_2$ and $Mo_1S_3Mo_2$ planes. [g] Distance between two capped sulfur atoms in the open face of bicapped tetrahedron.

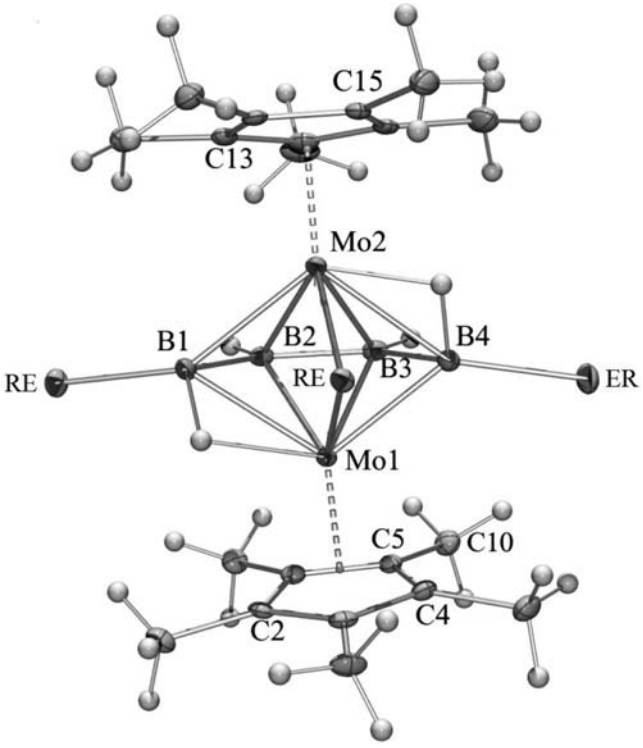

Figure 4. Molecular structure of **7** and **8** (Mo−Mo bond and aryl groups are not shown for clarity). Selected interatomic distances (Å) and angles (deg): **7**: Mo(1)−Mo(2) 2.6941(6), Mo(1)−B(1) 2.291(6), Mo(1)−B(2) 2.302(6), Mo(1)−B(3) 2.285(6), Mo(1)−B(4) 2.381(6), Mo(2)−B(1) 2.232(6), Mo(2)−B(2) 2.246(6), Mo(2)−B(3) 2.299(6), Mo(2)−B(4) 2.345(6), Mo(1)−S(3) 2.5234(14), Mo(2)−S(3) 2.4676(13), B(1)−B(2) 1.752(9), B(2)−B(3) 1.626(9), B(1)−S(1) 1.835(6), B(4)−S(2) 1.888(6); B(3)−Mo(1)−B(1) 82.0(2), Mo(2)−S(3)−Mo(1) 65.33(4). **8**: Mo(1)−Mo(2) 2.7081(3), Mo(1)−B(1) 2.339(3), Mo(1)−B(2) 2.244(3), Mo(1)−B(3) 2.228(4), Mo(1)−B(4) 2.195(3), Mo(2)−B(1) 2.366(3), Mo(2)−B(2) 2.259(3), Mo(2)−B(4) 2.300(3), Mo(1)−Se(1) 2.6065(4), Mo(2)−Se(1) 2.6677(4), B(2)−B(3) 1.647(5), B(4)−Se(3) 1.988(3), B(1)−Se(2) 2.005(3); B(4)−Mo(1)−B(3) 46.80(12), Mo(1)−Se(1)−Mo(2) 61.77(10).

lowered, the resonance at $\delta = -6.58$ ppm (two Mo−H−B) splits into two distinct peaks at $\delta = -6.20$, and −6.75 ppm in a 1:1 ratio (Figure 5). Thus, there are three different types of bridging protons which are connected to distinct boron atoms. Two of the Mo−H−B protons bridge the open face boron atoms, while the other one is bonded to the tetrahedral core (Mo_2B_2). Not all of the bridging hydrogen atoms of molecules **7** and **8** have been positioned by X-ray diffraction studies; however, their connectivity with regard to the metal and boron atoms (Scheme 1), has been confidently determined by low temperature $^1H\{^{11}B\}$ NMR and $^1H\{^{11}B\}$-$^{11}B\{^1H\}$ HETCOR spectra (Figure 5).

As shown in Table 2, the structural parameters and chemical shift values of **6**−**8** and their Cr, Re and Ta analogues exhibit several contrasting features. The M−M distances in **6**−**8** are shorter, but the average M−B distances are markedly longer. The distance between the two capping boron atoms differ to some extent with respect to the size of the open face of the cluster, which is more open in the Mo system. The ^{11}B resonances, on going from the lighter to the heavier metal atom, appeared at low field. The ^{77}Se NMR of **8** shows two resonances, one at $\delta = 461$ ppm for the bridged μ_2-SePh and another more upfield one at $\delta = 327$ ppm for the cage B-SePh group. The average B−Se bond length in **8** is longer comparable to that observed in $[(Cp^*Mo)_2B_4H_4Se_2]$.[27] However, they are significantly shorter when compared to those observed in other selenaborane clusters.[4b,e,5d,5e] This may be due to the tendency of the boron and selenium atoms to form polarized bonds that have a localized two-center character resulting in the observed distances.[28]

Conclusion

These results and others[6,29] demonstrate that many transient metallaborane intermediates can be stabilized by bridged chalogenide ligands. Thus, the isolation and structural characterization of compounds **6**−**8** provided the first direct evidence of the existence of intermediate **2**, a proposed unstable intermediate in the formation of $[(Cp^*Mo)_2B_5H_9]$. Although analogous insertions into transition metal−boron bonds have also been claimed, to our knowledge compounds **3** and **6**−**8** are the first structurally characterized products of such an insertion. It should also be noted that some of the byproducts generated by these reactions employing dichalcogenide as reactant were $[(Cp^*MoS)_2(\mu\text{-}\eta^1\text{-}S)_2]$, $[(Cp^*MoO)_2(\mu\text{-}S_2)]$, $[(Cp^*Mo)_2(\mu\text{-}S_2)(\mu\text{-}\eta^1\text{-}SPh)_2]$, or $[(Cp^*MoSe)_2(\mu\text{-}\eta^1\text{-}Se)_2]$.[30] This observation suggests that metallaborane reactions may be of use in the future not only for the synthesis

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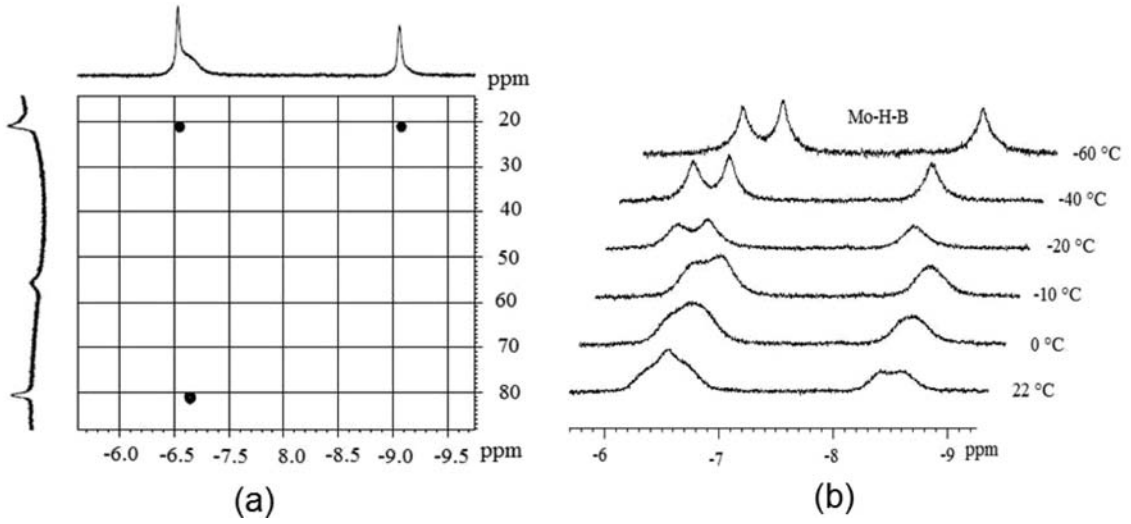

Figure 5. (a) $^{1}H\{^{11}B\}$-$^{11}B\{^{1}H\}$ HETCOR and (b) Variable-temperature $^{1}H\{^{11}B\}$ NMR of **8** in [D_8]toluene.

of new types of metallaheteroborane clusters but also for the preparation of other transition-metal main-group heteronuclear clusters.[31−36] The factors that lead to such insertion rather than a direct π-coordination to dichalcogen bonds are not yet understood. Further, systematic reactivity studies combined with theoretical treatments are required to fully understand these systems. Such work is in progress.

Experimental Section

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. MeI was freshly distilled prior to use. All other reagents Cp*H, $Mo(CO)_6$, BuLi, $LiBH_4$ in tetrahydrofuran (THF, Aldrich) were used as received. $[Cp^*MoCl_4]$[37] and the external reference, $[Bu_4N(B_3H_8)]$,[38] for the ^{11}B NMR were synthesized by the literature method. The dichalcogenide ligands Ph_2S_2,[39] $(PhCH_2)_2S_2$,[39] Ph_2Se_2,[40] and $[(2,6\text{-}(^tBu)_2\text{-}C_6H_2OH)_2S_2]$[41] were prepared as described in the literature. Chromatography was carried out on 3 cm of silica gel in a 2.5 cm diameter column. TLC was carried on 250 mm diameter aluminum-supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometers. Residual solvent protons were used as reference (δ, ppm, 22 °C, $CDCl_3$, 7.26), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in C_6D_6 (δ_B, ppm, −30.07) was used as an external reference for ^{11}B NMR spectra. Microanalyses for C, H, and N were performed on Perkin Elimer Instruments series II model 2400. 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.

Synthesis of 3−8. In a Flame-dried Schlenk tube, $[Cp^*MoCl_4]$, (0.5 g, 1.34 mmol) was suspended in toluene (20 mL) and cooled to −70 °C. $LiBH_4$·thf (4.02 mL, 8.05 mmol) was added via syringe, and the reaction mixture was warmed slowly over 20 min to room temperature and left stirring for an additional hour. The solvent was evaporated under vacuum, and the residue extracted into hexane. The yellowish green hexane extract was thermolyzed at 90 °C with excess of diphenyldisulfide PhS-SPh (1.17 g, 5.36 mmol) for 20 h. The solvent was removed in vacuo, and the residue was extracted into hexane. After removal of solvent from the filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with hexane/CH_2Cl_2 (95:05 *v*/*v*) yielded brown $[(Cp^*Mo)_2(\mu\text{-}\eta^1\text{-}SPh)_2(\mu_3\text{-}S)(H_2BSPh)]$, **3** (0.06 g, 5%) and $[(Cp^*Mo)_2B_5H_8(SPh)]$, **4** (0.08 g, 9%). Under the same reaction conditions, PhSe-SePh (1.67 g, 5.36 mmol) yielded $[(Cp^*Mo)_2B_5H_8(SePh)]$, **5** (0.07 g, 7%) and $[(Cp^*Mo)_2B_4H_5(SePh)_2(\mu\text{-}\eta^1\text{-}SePh)]$, **8** (0.18 g, 14%). Further, in a similar fashion, other dichalogenide ligands, for example, $PhCH_2S\text{-}SCH_2Ph$ (1.32 g, 5.36 mmol) and $(2,6\text{-}(^tBu)_2\text{-}C_6H_2OH)_2S_2$ (2.54 g, 5.36 mmol) provided $[(Cp^*Mo)_2B_2S_2H_2(\mu\text{-}\eta^1\text{-}S)]$, **6** (0.11 g, 14%) and $[(Cp^*Mo)_2B_2H_5(BSR)_2(\mu\text{-}\eta^1\text{-}SR)$, **7** (0.18 g, 11%, R = $2,6\text{-}(^tBu)_2\text{-}C_6H_2OH$), respectively.

Note that compound $[(Cp^*Mo)_2B_5H_9]$ was isolated as a major product in all cases and characterized by comparison of its spectroscopic data with those reported earlier.[9]

3: MS (ESI^+) *m*/*z*: 834 (isotopic pattern for 2Mo, 1B, 4S atoms); ^{11}B NMR: $\delta = -17.7$ (t, $J_{B-H} = 139$ Hz, 1B); ^{1}H NMR: $\delta = 7.78 - 6.86$ (m, 15H, 3Ph), 1.74 (s, 30H, 2Cp*), −11.50 (partially collapsed quartet (pcq), 2Mo-*H*-B); ^{13}C NMR: $\delta =$ 134.04, 133.54, 128.56, 128.02, 125.91 (s, $\underline{C}_6H_5$), 103.29 (s, $\eta^5\text{-}\underline{C}_5Me_5$), 12.29 (s, $\eta^5\text{-}C_5\underline{Me}_5$); IR (hexane, cm^{-1}): 459 m (Mo−S−Mo); elemental analysis calcd (%) for $C_{38}H_{47}BMo_2S_4$: C 54.68, H 5.68; found: C 55.33, H 5.81.

4: MS (FAB) P^+(max): *m*/*z* (%) 634 (isotopic pattern for 2Mo, 5B, 1S atoms); ^{11}B NMR: $\delta = 62.1$ (br, 1B), 61.5 (d, $J_{B-H} = 133$ Hz,

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Table 3. Crystallographic Data for Compounds **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
formula	$C_{38}H_{47}BS_4Mo_2.0.5CH_2Cl_2$	$C_{26}H_{43}B_5SMo_2$	$C_{26}H_{43}B_5SeMo_2$	$C_{40}H_{62}B_2Mo_4S_7$[a]	$C_{69}H_{90}Mo_2B_4S_3O_3$	$C_{38}H_{51}B_4Se_3Mo_2$
formula weight	877.15	633.59	680.49	1170.68[b]	1298.71	979.79
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_1/c$	$P2_1/c$
a (Å)	10.6733(3)	10.198(2)	10.3687(3)	12.744(5)	10.6528(2)	20.1362(14)
b (Å)	11.8836(4)	11.376.(2)	11.3702(3)	14.785(5)	27.0706(6)	11.4533(4)
c (Å)	17.4329(6)	13.934(3)	13.8112(4)	14.632(5)	25.9190(6)	17.2837(13)
α (deg)	71.821(2)	111.15(3)	110.2440(10)	90.000(5)	90.00	90.00
β (deg)	82.061(2)	104.01(3)	104.4370(10)	95.380(5)	100.631(2)	106.944(9)
γ (deg)	65.939(2)	92.30(3)	92.3050(10)	90.000(5)	90.00	90.00
V (Å^3)	1918.09(11)	1448.2(5)	1465.03(7)	2744.8(17)	7346.2 (3)	3818.0(4)
Z	2	2	2	2	4	4
D_{calc} (Mg/m^3)	1.519	1.453	1.543	1.416	1.174	1.707
F (000)	898	648	684	1180	2720	1940
μ (mm^{-1})	0.968	0.952	2.112	1.183	0.467	3.548
θ rRange (deg)	1.23−28.34	1.63−28.37	1.64−28.29	1.40−25.00	3.29−25.00	3.27−25.00
goodness-of-fit	1.021	1.056	0.901	1.486	0.893	0.891
R indices [$I > 2\sigma(I)$]	R1 = 0.0460 wR2 = 0.1015	R1 = 0.0341 wR2 = 0.0743	R1 = 0.0269 wR2 = 0.0676	R1 = 0.0932 wR2 = 0.3123	R1 = 0.0512 wR2 = 0.1251	R1 = 0.0208 wR2 = 0.0409
R indices (all data)	R1 = 0.0753 wR2 = 0.1153	R1 = 0.0461 wR2 = 0.0814	R1 = 0.0375 wR2 = 0.0745	R1 = 0.1123 wR2 = 0.3482	R1 = 0.0979 wR2 = 0.1338	R2 = 0.0319 wR2 = 0.0419
largest difference in peak and hole (e/ Å^3)	1.530 and −1.543	0.707 and −1.141	1.137 and −0.972	3.447 and −1.503	1.456 and −0.653	0.481 and −0.384

[a] Sum of the two chemical formula of ($C_{20}H_{32}S_3B_2Mo_2$) and ($C_{20}H_{30}S_4Mo_2$). [b] Sum of the two formula masses of **6** and $C_{20}H_{30}S_4Mo_2$.

2B), 34.2 (s, 1B), 24.2 (br, 1B); ^{1}H NMR: δ = 7.34−6.98 (m, 5H, Ph), 5.72 (br, 1BH$_t$), 5.24 (br, 1BH$_t$), 4.67 (br, 1BH$_t$), 3.21 (br, 1BH$_t$), 1.97 (s, 30H, 2Cp*), −5.70 (pcq, 2Mo-*H*-B), −6.87 (br, 2Mo-*H*-B); ^{13}C NMR: δ = 130.03, 128.32, 123.85 (s, *C*$_6$H$_5$), 107.97 (s, η^5-*C*$_5$Me$_5$), 12.60 (s, η^5-C$_5$*Me*$_5$); IR (hexane, cm^{-1}): 2461w, 2490w (BH$_t$); elemental analysis calcd (%) for $C_{26}H_{43}B_5Mo_2S$: C 49.28, H 6.84; found: C 48.53, H 6.68.

5: MS (FAB) P$^+$(max): m/z (%) 680 (isotopic pattern for 2Mo, 5B, Se atoms); ^{11}B NMR: δ = 64.14 (br, 1B), 62.4 (br, 1B), 59.8 (d, J_{B-H} = 133 Hz, 1B), 30.7 (s, 1B), 24.7 (br, 1B); ^{1}H NMR: δ = 7.48−7.01 (m, 5H, Ph), 5.69 (br, 1BH$_t$), 5.29 (br, 1BH$_t$), 4.21 (br, 1BH$_t$), 3.21 (br, 1BH$_t$), 2.33 (s, 30H, 2Cp*), −5.77 (pcq, 2Mo-*H*-B), −7.12 (br, 2Mo-*H*-B); ^{13}C NMR: δ = 132.30, 128.46, 124.59, (s, *C*$_6$H$_5$), 108.84 (s, η^5-*C*$_5$Me$_5$), 12.58 (s, η^5-C$_5$*Me*$_5$); IR (hexane, cm^{-1}): 2464w, 2480w, (BH$_t$); elemental analysis calcd (%) for $C_{26}H_{43}B_5Mo_2Se$: C 45.89, H 6.37; found: C 46.10, H 6.29.

6: MS (ESI$^+$) m/z: 582 (isotopic pattern for 2Mo, 2B, 3S atoms); ^{11}B NMR: δ = 18.8 (d, J_{B-H} = 133 Hz, 2B); ^{1}H NMR: δ = 3.80 (br, 2B−H$_t$), 2.18 (s, 30H, 2Cp*). ^{13}C NMR: δ = 111.8, (s, η^5-*C*$_5$Me$_5$), 13.71, (s, η^5-C$_5$*Me*$_5$); IR (hexane, cm^{-1}): 2493s (B−H$_t$), 474 m (Mo−S−Mo); elemental analysis calcd (%) for $C_{40}H_{62}B_2Mo_4S_7$: C 40.97, H 5.33; found: C 41.62, H 5.44.

7: MS (ESI$^+$) m/z: 1222 (isotopic pattern for 2Mo, 4B, 3S, 3O atoms); ^{11}B NMR: δ = 83.4 (d, J_{B-H} = 134 Hz, 1B), 49.8 (br, 1B), 30.45 (s, 2B); ^{1}H NMR: δ = 7.51−7.03 (m, 6H, C$_6$*H*$_2$OH), 5.00 (s, 3H, C$_6$H$_2$O*H*), 4.39, (br, 1B−H$_t$), 3.58 (br, 1B−H$_t$), 1.82 (s, 15H, Cp*), 1.64 (s, 15H, Cp*), 1.35−1.47 (s, 54H, 6(*CH*$_3$)$_3$C), −7.00 (br), Mo-*H*-B), −7.28 (br, Mo-*H*-B), −7.55 (br, Mo-*H*-B); ^{13}C NMR: δ = 135.40, 131.75, 129.80 (s, *C*$_6$H$_2$OH), 107.65, 106.35 (s, η^5-*C*$_5$Me$_5$), 34.69, 34.49, 34.41 (s, -*C*(CH$_3$)$_3$), 30.56, 30.30, 30.14 (s, C(*CH*$_3$)$_3$), 12.27, 11.95 (s, η^5-C$_5$*Me*$_5$); IR (hexane, cm^{-1}): 2476w (B−H$_t$), 459 (s Mo-*S*(R)-Mo, R = 2,6-(^{t}Bu)$_2$-C$_6$H$_2$OH); elemental analysis calcd (%) for $C_{62}H_{98}B_4Mo_2O_3S_3$: C 60.90, H 8.08; found: C 59.97, H 8.19.

8: MS (FAB) P$^+$(max): m/z (%): 979 (isotopic pattern for 2Mo, 4B, 3Se atoms); ^{11}B NMR: δ = 78.8 (br, 1B), 54.0 (br, 1B), 19.2 (s, 2B); ^{1}H NMR: δ = 7.48−6.78 (m, 15H, C$_6$*H*$_5$), 4.86 (br, 1B−H$_t$), 4.54 (br, 1B−H$_t$), 2.21 (s, 15H, Cp*), 1.80 (s, 15H, Cp*), −6.58 (br, 2Mo-*H*-B), −8.58 (br, Mo-*H*-B); ^{13}C NMR: δ = 134−128, (s, *C*$_6$H$_5$), 108.38, 107 (s, η^5-*C*$_5$Me$_5$), 12.82, 11.79 (s, η^5-C$_5$*Me*$_5$); ^{77}Se NMR: δ = 327 (s, 2Se), 461 (s, Se); IR (hexane, cm^{-1}): 2476w (B−H$_t$); elemental analysis calcd (%) for $C_{38}H_{50}B_4Mo_2Se_3$: C 46.63, H 5.15; found: C 47.17, H 5.25.

X-ray Structure Determination. Suitable X-ray quality crystals of **3**−**8** were grown by slow diffusion of a hexane/CH_2Cl_2 (9.5:0.5 v/v) solution and single crystal X-ray diffraction studies were undertaken (Table 3). Crystal data for **3**−**6** were collected and integrated using Bruker AXS (Kappa Apex II) and for **7** and **8** using Oxford Diffraction Xcalibur-S CCD system diffractometer equipped with graphite monochromated Mo−Kα (λ = 0.71073 Å) radiation at 150 K. The structure was solved by heavy atom methods using SHELXS-97[42] and refined using SHELXL-97[43] (Sheldrick, G.M., University of Göttingen).

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Supporting Information Available: The supplementary crystallographic data and X-ray crystallographic files for **3**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

(42) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

(43) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.