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Chlorinated Hypoelectronic Dimetallaborane Clusters: Synthesis, Characterization, and Electronic Structures of $(\eta^5\text{-}C_5Me_5W)_2B_5H_nCl_m$ (n = 7, m = 2 and n = 8, m = 1)

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Pyrolysis of $(\eta^5\text{-}C_5Me_5WH_3)B_4H_8$, **1**, in the presence of excess $BHCl_2 \cdot SMe_2$ in toluene at 100 °C led to the isolation of $(\eta^5\text{-}C_5Me_5W)_2B_5H_9$, **2**, and B—Cl inserted $(\eta^5\text{-}C_5Me_5W)_2B_5H_8Cl$, **3**, and $(\eta^5\text{-}C_5Me_5W)_2B_5H_7Cl_2$, **4**—**7** (four isomers). All the chlorinated tungstaboranes were isolated as red and air and moisture sensitive solids. These new compounds have been characterized in solution by ^1H, ^{11}B, ^{13}C NMR, and the structural types were unequivocally established by crystallographic analysis of compounds **3**, **4**, and **7**. Density functional theory (DFT) calculations were carried out on the model molecules of **3**—**7** to elucidate the actual electronic structures of these chlorinated species. On grounds of DFT calculations we demonstrated the role of transition metals, bridging hydrogens, and the effect of electrophilic substitution of hydrogens at B—H vertices of metallaborane structures.

Introduction

Electrophilic substitution of hydrogen at B—H vertices of the boranes or carboranes is a well-known reaction, and they have been studied for a variety of cluster types by Hawthorne[1−3] and others.[4−12] Such studies, which lead to perhalogenation, continue to be of significant interest as the perhalogenated carborane clusters bear potential applicability for a weakly coordinating anion.[13−16] Recently, Reed has demonstrated that carborane acids, a family of chlorinated carboranes, are a new class of protic acids notable for their "strong yet gentle" properties that allow the isolation of highly reactive cations, for examples, $HC_{60}{}^+$, $C_6H_7{}^+$, *t*-butyl cation, H_3O^+, $H_5O_2{}^+$, and so forth.[13] Although halogenation of carboranes and boranes are well documented, not many examples are known in metallaborane or in

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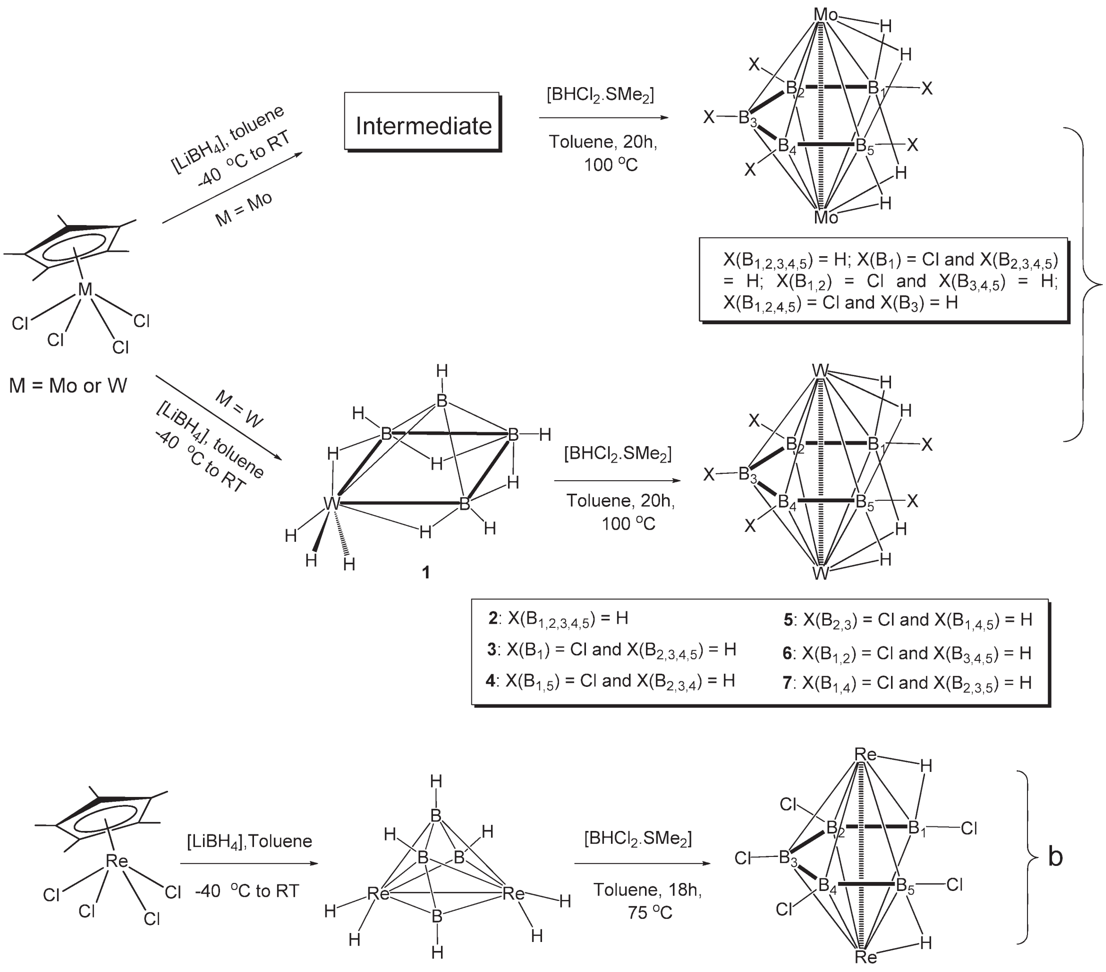
Scheme 1. (a) Synthesis of Chlorinated Molybda- and Tungstaboranes, and (b) Synthesis of Rhenaboranes[a]



[a] Cp* = (η^5-C_5Me_5) rings are not shown in the scheme for clarity.

metallacarborane chemistry.[17−20] We are particularly interested in B-functionalized metallaborane species, in particular halogenation of small metallaborane clusters, since these derivatives are important in preparing functionalized clusters for assembly into larger arrays, extended polymetallic clusters,[21] and B−B linked systems.[22−24]

After it had been discovered that the reaction of (η^5-$C_5Me_5ReH_2)_2B_4H_4$ with $BHCl_2 \cdot SMe_2$ led to the isolation of perchlorinated (η^5-$C_5Me_5Re)_2B_5Cl_5H_2$[17], a reinvestigation of related molybdenum and tungsten systems became of interest. As the results obtained from the pyrolysis of $BHCl_2 \cdot SMe_2$ and an in situ generated intermediate from (η^5-$C_5Me_5Mo)Cl_4$ and $LiBH_4$[25] (see Scheme 1), yielded (η^5-$C_5Me_5Mo)_2B_5Cl_4H_5$,[26] we have therefore pursued this chemistry in the tungsten system which offered only partial chlorination in the framework geometry. Hence, upon availability of these chlorinated species theoretical calculations using the density functional theory (DFT) methods were carried out to elucidate the electronic structures of these clusters. An examination of the electronic structure of the model molecules reveals the role of transition metals, bridging hydrogens, and the effect of electrophilic substitution of hydrogens at B−H vertices of metallaboranes. As will be seen, DFT calculations also show interesting correlation

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between the M−M bond length and the successive substitution of hydrogen by chlorine in **3**−**7**.

Results and Discussion

Synthesis and Characterization of $M_2B_5H_8Cl$ and $M_2B_5H_7Cl_2$ (M = η^5-C_5Me_5W). As shown in Scheme 1, (η^5-$C_5Me_5W)_2B_5H_8Cl$, **3**, and (η^5-$C_5Me_5W)_2B_5H_7Cl_2$, **4**−**7** (four isomers), were isolated from the pyrolysis of (η^5-$C_5Me_5WH_3)B_4H_8$, **1** with excess of $BHCl_2 \cdot SMe_2$. The composition and structures of **3**−**7** are established from the mass spectral analysis and by multinuclear NMR spectroscopy, and in the case of **3**, **4**, and **7** by X-ray structure determination. Compounds **4** and **5** were isolated as a mixture of two isomers, and all of our attempts to separate these two isomers were not successful because of similar polarities as well as low stabilities on thin layer chromatography. Descriptions of the characterizations of **3**−**7** from mass spectrometric, NMR, and X-ray diffraction studies follow.

The mass spectrometric data of **3** suggests a molecular formula of $C_{20}H_{38}W_2B_5Cl$. This formulation of **3** rationalizes the presence of five ^{11}B resonances in the ratio of 1:1:1:1:1 where the resonance at δ = 45.1 ppm showed no coupling in ^{11}B NMR confirms the B−Cl environment. Similarly, the $^1H\{^{11}B\}$ NMR spectrum also reveals three types of B−H protons in the ratio of 2:1:1 and the presence of two kinds of W−H−B protons each at δ = −6.79 and −7.79 ppm of intensity two respectively.

Single crystals suitable for X-ray diffraction analysis of **3** were obtained from a hexane solution at −4 °C, thus allowing the structural characterization of (η^5-$C_5Me_5W)_2B_5H_8Cl$ and confirm the structural inferences made on the basis of spectroscopic results. The molecular structure of **3** in the solid state is shown in Figure 1, where this compound is seen to be a cluster analogue of (η^5-$C_5Me_5M)_2B_5H_9$, (M = Cr,[27] Mo,[28] and W[29]) and (η^5-$C_5Me_5ReH)_2B_5Cl_5$,[17] with which it is isoelectronic. Superficially this structure resembles a hexagonal bipyramid with a single missing equatorial vertex but, given the electron count of six skeleton electron pairs (seps), is probably more accurately thought of as a bicapped trigonal bipyramid. A similar structural interpretation has been suggested for (η^5-$C_5H_4MeMo)_2$-B_5H_9[28a] and in case the trigonal bipyramidal $M_2B_3H_3$ unit is capped by two BH_3 units over the M_2B faces. The average intra-cluster B−B and W−B bond distances of 1.72 Å and 2.25 Å, respectively, and W−W bond length of 2.8215(3) Å in **3** are comparable to those of observed in (η^5-$C_5Me_5W)_2B_5H_9$.[29]

The second red compounds, **4** and **5**, have been isolated following thin layer chromatography (TLC) in 8% yield as the mixture of two products roughly in a ratio of 60:40. The mass spectrum of the mixture showed a single parent ion envelope, suggesting the presence of two geometrical isomers containing two Cl substitution at B−H terminal proton. 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 having a plane of symmetry contains three kinds of boron resonances with an intensity ratio of 2:2:1, and the other set contains five kinds of boron resonances with an intensity ratio of 1:1:1:1:1. The broad resonances at δ = 64.4 and 42.7 and 42.6 ppm have been assigned to the boron atoms containing chlorine. Furthermore, the ^1H NMR spectrum of each set clearly shows the presence of B−H, Cp*, and W−H−B proton resonances. Suitable crystals of one of these isomers, **4**, for structure determination were obtained by cooling a concentrated hexane solution to −10 °C.

The solid state single crystal X-ray diffraction structure of **4**, shown in Figure 2, confirms the structural inferences

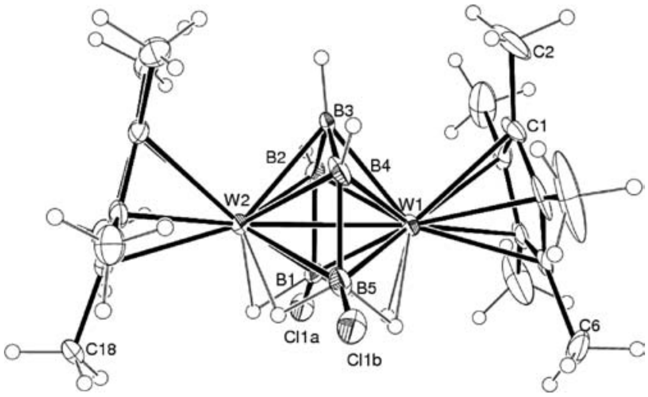

Figure 1. Molecular structure of (η^5-$C_5Me_5W)_2B_5H_8Cl$, **3**. Thermal ellipsoids have been drawn at the 30% probability level. Relevant bond lengths [Å] and angles [deg]: W(1)−W(2) 2.8215(3), W(1)−B(1) 2.285(7), W(1)−B(2) 2.221(7), W(1)−B(3) 2.195(6), W(1)−B(4) 2.232(7), W(1)−B(5) 2.297(7), W(2)−B(1) 2.302(6), W(2)−B(2) 2.224(6), W(2)−B(3) 2.201(6), W(2)−B(4) 2.239(8), W(2)−B(5) 2.307(8), B(1)−B(2) 1.743(9), B(2)−B(3) 1.702(10), B(3)−B(4) 1.695(10), B(4)−B(5) 1.743(10); W(1)−B(1)−W(2) 75.9(2), W(1)−B(4)−W(2) 78.3(2), W(1)−B(5)−W(2) 75.6(2), B(1)−Cl(1a) 1.818(7).

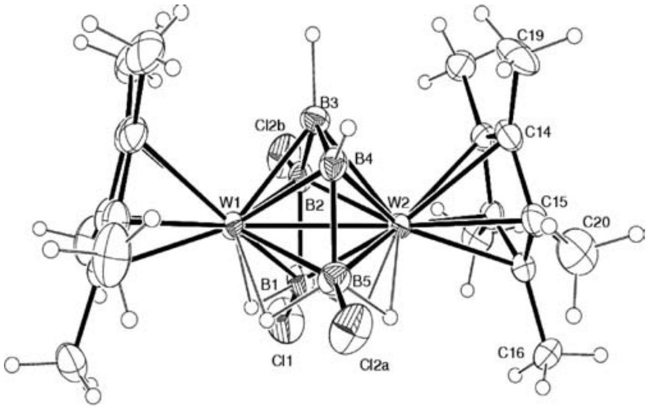

Figure 2. Molecular structure of (η^5-$C_5Me_5W)_2B_5H_7Cl_2$, **4**. Thermal ellipsoids have been drawn at the 30% probability level. Relevant bond lengths [Å] and angles [deg]: W(1)−W(2) 2.8313(3), W(1)−B(1) 2.289(8), W(1)−B(2) 2.212(7), W(1)−B(3) 2.194(8), W(1)−B(4) 2.228(8), W(1)−B(5) 2.289(9), W(2)−B(1) 2.295(8), W(2)−B(2) 2.233(8), W(2)−B(3) 2.218(8), W(2)−B(4) 2.229(7), W(2)−B(5) 2.311(8), B(1)−B(2) 1.740(12), B(2)−B(3) 1.678(12), B(3)−B(4) 1.700(11), B(4)−B(5) 1.739(12); W(1)−B(1)−W(2) 76.3(2), W(1)−B(2)−W(2) 79.1(3), W(1)−B(4)−W(2) 78.9(3), W(1)−B(5)−W(2) 76.0(3), B(1)−Cl(1) 1.823(8).

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made on the basis of spectroscopic results. The presence of Cl2a and Cl2b in Figure 2 shows that the compound **4** (81%) cocrystallizes with a minor isomeric component of compound **6** (19%). The average intra-cluster B−B and W−B bond distances of 1.71 Å and 2.25 Å, respectively, are comparable to those observed in $(\eta^5\text{-}C_5Me_5W)_2B_5H_9$;[29] however, the W−W bond length of 2.8313(3) Å is a little longer as compared to that in **3**.

The third red product, **6**, has been isolated in 10% yield. The composition of **6** is recognized from the mass spectral analysis together with multinuclear NMR spectroscopy. The mass spectrum of the compound showed a single parent ion corresponding to $C_{20}H_{37}B_5W_2Cl_2$ which is consistent with a formula containing five B, two Cl, and two W atoms. Further, the parent ion mass of 769 supports addition of two Cl atoms to the $(\eta^5\text{-}C_5Me_5W)_2B_5H_9$ framework. On the other hand, the ^{11}B and ^1H NMR data of **6** are very similar to that of $(\eta^5\text{-}C_5Me_5Mo)_2B_5H_7Cl_2$[26] in which two chlorine atoms are at the 1 and 2 positions (Scheme 1a).

The fourth red product, **7**, has been isolated following TLC in 4% yield. From the mass spectral analysis combined with the ^{11}B NMR spectra, compound **7** is formulated as $(\eta^5\text{-}C_5Me_5W)_2B_5H_7Cl_2$. The ^{11}B NMR spectrum of **7** shows five boron resonances in the ratio of 1:1:1:1:1, two of which are singlet in the ^{11}B NMR which confirms the presence of two B−Cl units. Beside the Cp* protons, the ^1H NMR spectrum of **7** also reveals three B−H protons in the ratio of 1:1:1 and the presence two kinds of W−H−B protons at $\delta = -6.66$ and -7.42 ppm, respectively.

Single crystals suitable for X-ray diffraction analysis of **7** were obtained from a hexane solution at −5 °C, thus allowing for the structural characterization. The molecular structure of **7**, shown in Figure 3, shows a bicapped *closo* trigonal bipyramidal geometry isostructural with **3** and **4**. The presence of Cl2a, Cl2b, and Cl2c in Figure 3 shows that the compound **7** (65%) cocrystallizes with a minor isomeric component of compound **4** (12%) and the corresponding 1,3 isomer (23%). The W−B bond lengths of **7** range from 2.21 Å to 2.33 Å, and the B−B distances range from 1.70 Å to 1.76 Å and are similar to those observed in **3** and **4**. These findings, together with the theoretical data (vide infra), lend further support to the description of the metal−metal linkage in such chlorinated species as a rather weaker bond than the unchlorinated species, $(\eta^5\text{-}C_5Me_5W)_2B_5H_9$.

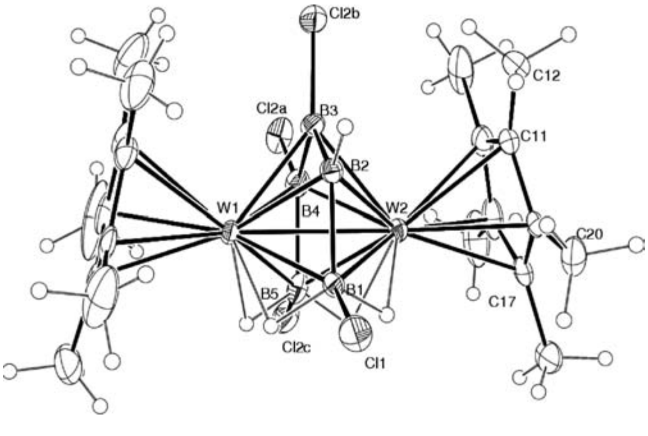

Figure 3. Molecular structure of $(\eta^5\text{-}C_5Me_5W)_2B_5H_7Cl_2$, **7**. Thermal ellipsoids have been drawn at the 30% probability level. Relevant bond lengths [Å] and angles [deg]: W(1)−W(2) 2.8301(3), W(1)−B(1) 2.295(7), W(1)−B(2) 2.229(7), W(1)−B(3) 2.212(7), W(1)−B(4) 2.223(7), W(1)−B(5) 2.314(7), W(2)−B(1) 2.316(6), W(2)−B(2) 2.226(6), W(2)−B(3) 2.217(7), W(2)−B(4) 2.228(7), W(2)−B(5) 2.329(7), B(1)−B(2) 1.742(9), B(2)−B(3) 1.700(9), B(3)−B(4) 1.718(10), B(4)−B(5) 1.760(11); W(1)−B(1)−W(2) 75.72(19), W(1)−B(2)−W(2) 78.9(2), W(1)−B(4)−W(2) 79.0(2), W(1)−B(5)−W(2) 75.1(2), B(1)−Cl(1) 1.813(6), B(4)−Cl(2a) 1.813(7).

Computational Studies

Earlier Fehlner has shown that chloromonoboranes, $BH_2Cl\cdot SMe_2$ and $BHCl_2\cdot SMe_2$, are effective in inserting borane fragments into metallaboranes with different rates than found for $BH_3\cdot THF$.[17−19] Thus, reaction of $(\eta^5\text{-}C_5Me_5ReH_2)_2B_4H_4$ with $BHCl_2\cdot SMe_2$ led to the isolation of $(\eta^5\text{-}C_5Me_5ReH)_2B_5Cl_5$ not observed on reaction with $BH_3\cdot THF$. The perchlorinated rhenaborane, $(\eta^5\text{-}C_5Me_5ReH)_2B_5Cl_5$ constitutes the first example of a dimetallaborane fully chlorinated at boron. However, as discussed above, reaction of $(\eta^5\text{-}C_5Me_5WH_3)B_4H_8$ with $BHCl_2\cdot SMe_2$ offers only partial chlorination in the framework geometry. Hence, theoretical calculations using the density functional theory (DFT) methods were carried out on the model complexes **3**−**7** with Cp $(\eta^5\text{-}C_5H_5)$ ligands instead of Cp* ligands. The model of the electronic structure that develops provides the electronic origins of the novel observed structures and demonstrates the factors behind the substitution patterns.

All the calculations were done using Gaussian 03 suite of programs.[30] Full geometry optimizations were done and subsequent Hessians were calculated by using Becke's 3-parameter hybrid exchange functional[31,32] in combination with the nonlocal correlation functional provided by the Lee−Yang−Parr expression,[33] B3LYP. The basis set used was LANL2DZ.[34] To support the experimental data of isomers **4**−**7** we have calculated the ^{11}B and ^1H NMR chemical shifts using the GIAO method at the B3LYP level of theory using the LANL2DZ basis set. The computed values are shown in Table 1. The ^1H NMR shifts have shown a systematic deviation, and a proper scaling factor would give more appropriate results. Alternatively employing higher basis sets would also improve the results although it increases the computational costs.

Isodesmic Equations. During the chlorination of $(MCp^*)_2B_5H_{7+x}$, ($x = 2$ when M = Mo and W; $x = 0$ when M = Re) a rapid perchlorination is observed in the rhenium system;[17] in the molybdenum system the maximum number chlorine

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Table 1. Calculated ^{11}B and ^{1}H NMR Chemical Shifts (δ, ppm) for **3**−**7** Compared with the Corresponding Experimental Chemical Shifts[a]

		3		4		5		6		7	
	atom	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
^{11}B NMR	B1	45.1	40.4929	42.6	37.9202	28.6	19.8707	43.2	39.2239	38.5	40.7119
	B2	50.6	48.7815	46.2	44.5386	42.7	62.7885	65.4	64.8359	44.4	44.4918
	B3	44.1	44.3739	50.3	40.8604	64.4	64.9202	43.2	41.7814	46.1	43.4236
	B4	42.6	40.1084	46.2	44.5353	39.5	40.8355	40.3	39.5483	60.5	61.3193
	B5	24.3	19.3041	42.6	37.9197	25.2	18.4563	23.4	19.4293	26.4	22.3556
^{1}H NMR	H1					6.59	−3.9937				
	H2	6.36	−3.3972	7.04	−3.782					6.41	−3.6808
	H3	3.69	−5.3851	3.55	−5.4009			4.39	−5.1495	5.65	−5.2861
	H4	6.36	−4.431	7.04	−3.782	6.03	−4.0016	6.02	−4.4789		
	H5	5.62	−3.963			4.58	−4.4038	5.68	−4.1431	6.43	−3.7463
^{1}H NMR	H$_{\mu}$1	−7.79	−14.4524	−6.47	−13.6685	−7.70	−14.9149	−7.57	−14.6389	−7.42	−14.0067
	H$_{\mu}$2	−7.79	−14.0059	−6.47	−13.6666	−7.70	−14.41	−7.57	−13.9484	−7.42	−13.5391
	H$_{\mu}$3	−6.69	−13.8191	−6.47	−13.6653	−7.39	−14.4078	−6.34	−13.9478	−6.66	−13.5648
	H$_{\mu}$4	−6.69	−14.4254	−6.47	−13.6643	−7.39	−14.9157	−6.34	−14.6404	−6.66	−13.9951

[a] $H_{\mu}1$ = W(1)−H−B(2), $H_{\mu}2$ = W(2)−H−B(2), $H_{\mu}3$ = W(1)−H−B(1), $H_{\mu}4$ = W(2)−H−B(1).

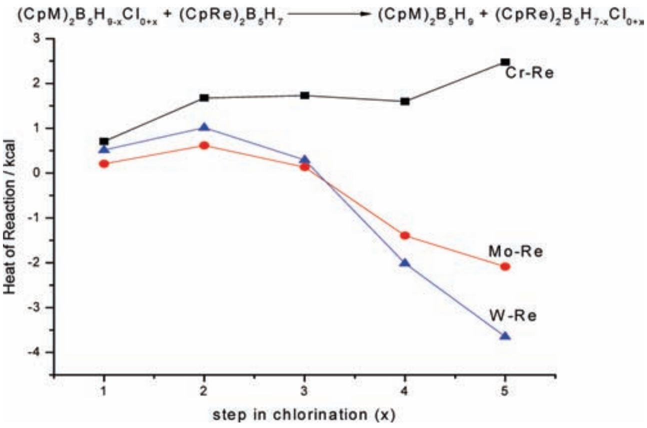

Figure 4. Heats of reaction in which the chlorines have been transferred from $(MCp)_2B_5H_xCl_y$ (M = Cr, Mo, W) to $(ReCp)_2B_5H_7$.

substitutions obtained was four; and in case of tungsten the maximum number is two. Here we made an attempt to study the influence of the transition metals on the chlorination of metallaborane clusters. Unfortunately, because of the lack of information on the nature of intermediates or transition states of the reactions we could not study the kinetic profile of the reaction. But the thermodynamic profiles were studied using the isodesmic equations. The results of the isodesmic equations, shown in Figure 4, suggest that the Cr system would provide more favorable conditions for chlorination than the Mo or W ones. Moreover, this study also suggests that $(Cp^*Cr)_2B_5H_9$ can be chlorinated completely if one were to attempt doing so.

It should be noted that the heats of reaction in the above-mentioned isodesmic equations are very low, and a study of the reaction mechanism and the kinetic profiles need to be done to unravel the mystery of metal influence in perchlorination of metallaboranes. Such a study would also throw light on the transition states and other intermediates in the reaction.

Structural Analysis. A previous study by Fehlner using Fenske−Hall molecular orbital calculations was carried out on $M_2B_4H_8$ and $M_2B_5H_9$ (M = Cp*Cr and Cp*Mo) systems to determine the electronic factors underlying the differences in stability between these two novel systems.[27] An argument based upon orbital overlap has been used to explain why a five membered middle ring is more stable than a four membered ring system. Here we have made a comparative study among $(ReCp)_2B_6H_6$(I), $(ReCp)_2B_5H_7$(II), and $(WCp)_2B_5H_9$(III) systems to understand two major structural differences, namely, (i) the opening of the middle ring and (ii) the bridging hydrogens. These structures can be viewed as distorted triple decker sandwich complexes and are extremely electron deficient, hypoelectronic metallaborane clusters.[35−37]

As illustrated in Figure 5, all the three molecules, I−III, have the equal electronic counts. When the MOs of $(ReCp)_2B_5H_7$ and $(WCp)_2B_5H_9$ are compared with $(ReCp)B_6H_6$, the most dramatic change observed is one of the π orbitals. This π orbital (67) in the closed system (I), as shown in Figure 6, is lowered in energy because of the interaction with the 1s orbital of the bridging hydrogens in structures II and III. Addition of hydrogens to the boron along the open faces of II and III increases the coordination number. This change influences the hybridization of the boron atoms and weakens the bond between the metal and boron (along the open face; Figure 7). One common feature among all these three structures is the strong M−M bonding which is facilitated by the large middle ring.

In principle the mno rule[38] could be applied to the above set of structures $(ReCp)_2B_6H_6$ (I), $(ReCp)B_5H_7$ (II), and $(WCp)_2B_5H_9$ (III) where the electron requirement of "$m + n + o + p$" for $(ReCp)_2B_6H_6$ (I) is 25 ($m = 3$, $n = 18$, $o = 2$, and $p = 2$; where m is the number of individual polyhedral fragment, n is the number of vertexes in the polyhedron, o is the number of single-vertex-sharing junctions, p is the number of missing vertexes in the idealized *closo* skeleton). The number of available electron pairs from two Cp rings and one B_6H_6 ring are 15 and 6 respectively. The contribution from the metal can be debated. Two Cp rings may be treated as Cp^{1-} in counting oxidation state and thus, one electron pair from the metal is obvious. The involvement of three additional electron pairs can be envisaged as the result of the stabilization of one σ^* and two π^* M−M orbitals by the corresponding π levels of B_6H_6 ring. Details of this will be discussed elsewhere.

Effect of Chlorine on Substitution of Hydrogen at B−H Vertices. The substituted chlorines which form exohedral bonds with the boron do not influence the skeletal bonding. Nevertheless because of the high electronegativity difference between Cl and B and the large size difference between Cl and H, substitution by chlorine affects the geometric parameters. We have focused on two structural parameters, for example, the radius of the middle ring and the metal−metal distance. The values of the two parameters for the most stable isomers are

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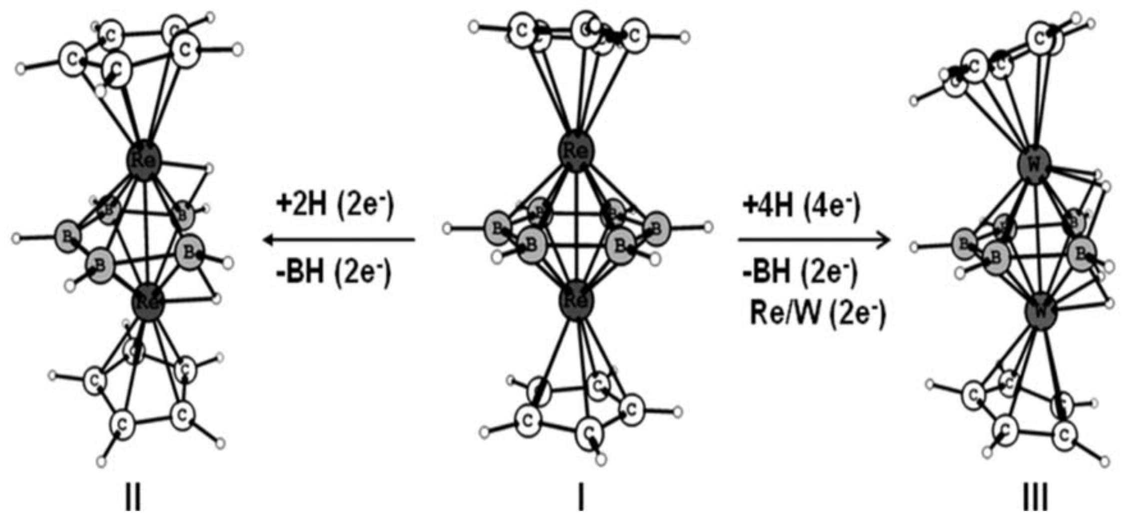

Figure 5. Schematic illustration of iso-electronic relationship between three triple-decker sandwich complexes (I−III).

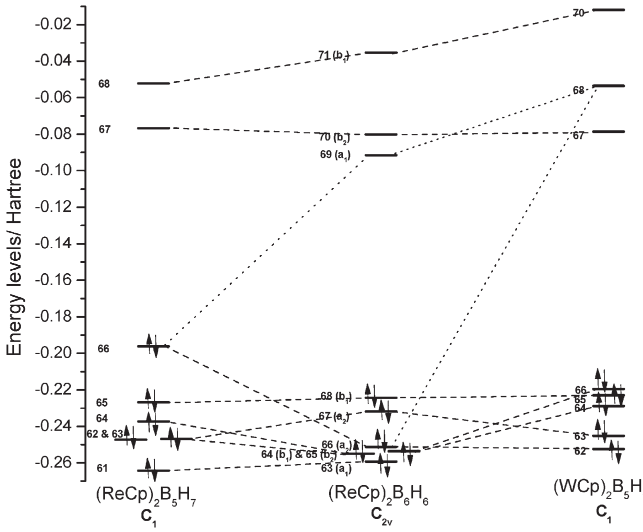

Figure 6. Correlation diagram for structures I−III.

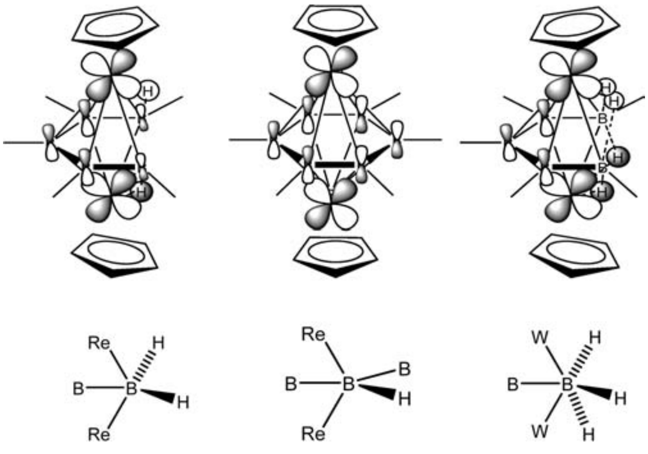

Figure 7. Stabilization of the M−M π^* orbital by the addition of bridging hydrogens. The coordination around the two boron atoms along the open faces is shown below.

tabulated in Table 2. On stepwise substitution of hydrogen in $(MCp)_2B_5H_9$ by chlorine the boron ring shrinks and the maximum occurred when perchlorinated. Subsequently, the metal−metal bond length increases, and a longest M−M distances is observed when all the B−H hydrogens are substituted. Such a ring and cage contraction behavior is also observed during our studies on chlorination of pure boron clusters. Furthermore, this observation is consistent with the fact that a larger ring facilitates a stronger and hence shorter metal−metal bond.[35]

Table 2. Middle Ring Perimeter and Corresponding M−M Distance As the Metallaborane Is Chlorinated[a]

		middle ring perimeter			metal−metal distance		
S. no.	systems	Cr	Mo	W	Cr	Mo	W
1	$(MCp)_2B_5H_9$	10.116	10.326	10.264	2.597	2.836	2.836
2	$(MCp)_2B_5H_8Cl$	10.096	10.307	10.239	2.601	2.849	2.849
3	$(MCp)_2B_5H_7Cl_2$	10.077	10.298	10.222	2.605	2.854	2.855
4	$(MCp)_2B_5H_6Cl_3$	10.070	10.305	10.226	2.608	2.858	2.861
5	$(MCp)_2B_5H_5Cl_4$	10.052	10.293	10.211	2.614	2.872	2.874
6	$(MCp)_2B_5H_4Cl_5$	10.043	10.298	10.208	2.619	2.879	2.881

[a] Parameters of the structures are found to be the global minima.

Conclusion

The reactivity of metallaboranes is significantly controlled by the metal center as observed in M_2B_4 frameworks.[39] Although $(\eta^5\text{-}C_5Me_5Cr)_2B_4H_8$ and $(\eta^5\text{-}C_5Me_5Re)_2B_4H_8$ have the same geometry they react in a different fashion with $BH_3{\cdot}THF$,[17] CO,[40] $BHCl_2{\cdot}SMe_2$,[17] and $Co_2(CO)_8$.[41] DFT study clearly reveals the distinctive role of the transition metal in predicting the reaction pathway with $BHCl_2{\cdot}SMe_2$. Further, metallaboranes with frameworks containing more bridging hydrogens often observed more reactive because of more open shapes; however, the reverse is observed in Re versus W chemistry. In this report we have shown that with more substitution of hydrogen by chlorination at B−H vertices in $(\eta^5\text{-}C_5Me_5M)_2B_5H_{7+x}$ (when M = Re, $x = 0$; M = Mo or W, $x = 2$) the center middle ring shrinks and

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makes the M−M bond longer. For example, the W−W bond length in the monochlorinated species is 2.82 Å while in the dichlorinated species it is 2.83 Å. Although we do not have any experimental data for the Cr system the theoretical results seem to indicate that more chlorination at B−H is favorable in the Cr system and is least favorable in the W system.

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. Cp*H, W(CO)$_6$, BuLi, BH$_3$·THF, BHCl$_2$·SMe$_2$, LiBH$_4$ in THF (Aldrich) were used as received. MeI was purchased from Aldrich and was freshly distilled prior to use. $(\eta^5\text{-C}_5\text{Me}_5)\text{WCl}_4$ was prepared with the literature method.[42] The external reference for the ^{11}B NMR, [Bu$_4$N(B$_3$H$_8$)], was synthesized with the literature method.[43] $(\eta^5\text{-C}_5\text{Me}_5\text{WH}_3)\text{B}_4\text{H}_8$ and $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_9$ were prepared as described previously.[29] 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 [Bu$_4$N(B$_3$H$_8$)] in C$_6$D$_6$ (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 mÅ) as the FAB gas.

Synthesis of $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_8\text{Cl}$, 3, and $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, 4−7. In a flame-dried Schlenk tube, $(\eta^5\text{-C}_5\text{Me}_5\text{WH}_3)\text{B}_4\text{H}_8$, **1** (0.5 g, 1.34 mmol) in 20 mL of toluene was heated with 5 fold excess of BHCl$_2$·SMe$_2$ (0.77 mL, 6.7 mmol) at 100 °C 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 of solvent from filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with hexane/CH$_2$Cl$_2$ (85:15 v/v) yielded orange $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_9$, **2** (0.14 g, 15%), red $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_8\text{Cl}$, **3** (0.12 g, 12%), red $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **4−5** (0.08 g, 8%, mixture of two isomers), red $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **6** (0.1 g, 10%), and red $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **7** (0.04 g, 4%).

Spectroscopic data for $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_8\text{Cl}$, **3**: MS (FAB) P$^+$(max): *m*/*z* (%) 734 (isotopic pattern for 2W, 1Cl, and 5B atoms); ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 50.6 (d, $J_{\text{B-H}}$ = 140 Hz, 1B), 45.1 (s, 1B−Cl), 44.1 (br, 1B), 42.6 (d, $J_{\text{B-H}}$ = 137 Hz, 1B), 24.3 (br, 1B); ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.36 (partially collapsed quartet (pcq), 2BH$_t$), 5.62 (pcq, 1BH$_t$), 3.69 (pcq, 1BH$_t$), 2.04 (s, 30H, Cp*), −6.79 (br, 2W−H−B), −7.79 (br, 2W−H−B); ^{13}C NMR (C$_6$D$_6$, 22 °C): δ 107.12 (s, η^5-C$_5$Me$_5$), 14.4 (s, CH$_3$ in η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2476w, 2440w (B−H$_t$).

Spectroscopic data for $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **4−5** *(combined NMR)*: MS (FAB) P$^+$(max): *m*/*z* (%) 769 (isotopic pattern for 2W, 2Cl, and 5B atoms); ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 64.4 (s, 1B−Cl), 50.3 (br, 1B), 46.2 (d, $J_{\text{B-H}}$ = 155 Hz, 2B), 42.7 (s, 1B−Cl), 42.6 (s, 2B−Cl), 39.5 (d, $J_{\text{B-H}}$ = 140 Hz, 1B), 28.6 (br, 1B), 25.2 (br, 1B); ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 7.04 (pcq, 2BH$_t$), 6.59 (pcq, 1BH$_t$), 6.03 (pcq, 1BH$_t$), 4.58 (pcq, 1BH$_t$), 3.55 (pcq, 1BH$_t$), 2.08 (s, 30H, Cp*), 1.99 (s, 30H, Cp*), −6.47 (br, 4W−H−B), −7.39 (br, 2W−H−B), −7.7 (br, 2W−H−B); ^{13}C NMR (C$_6$D$_6$, 22 °C): δ 106.23 (s, η^5-C$_5$Me$_5$), 106.11 (s, η^5-C$_5$Me$_5$), 12.65 (s, CH$_3$ in η^5-C$_5$Me$_5$), 12.43 (s, CH$_3$ in η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2496w, 2468w (B−H$_t$).

Spectroscopic Data for $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **6**: MS (FAB) P$^+$(max): *m*/*z* (%) 769 (isotopic pattern for 2W, 2Cl, and 5B atoms); ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 65.4 (s, 1B−Cl), 45.2 (br, 1B), 43.2 (s, 1B−Cl), 40.3 (d, $J_{\text{B-H}}$ = 143 Hz, 1B), 23.4 (br, 1B); ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.02 (pcq, 1BH$_t$), 5.68 (pcq, 1BH$_t$), 4.39 (pcq, 1BH$_t$), 1.99 (s, 30H, Cp*), −6.34 (br, 2W−H−B), −7.57 (br, 2W−H−B); ^{13}C NMR (C$_6$D$_6$, 22 °C): δ 105.26 (s, η^5-C$_5$Me$_5$), 11.10 (s, CH$_3$ in η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2479w, 2458w (B−H$_t$).

Spectroscopic Data for $(\eta^5\text{-C}_5\text{Me}_5\text{W})_2\text{B}_5\text{H}_7\text{Cl}_2$, **7**: MS (FAB) P$^+$(max): *m*/*z* (%) 769 (isotopic pattern for 2W, 2Cl, and 5B atoms); ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 60.5 (s, 1B−Cl), 46.1 (br, 1B), 44.4 (br, 1B), 38.5 (s, 1B−Cl), 26.4 (br, 1B); ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.43 (pcq, 1BH$_t$), 6.41 (pcq, 1BH$_t$), 5.65 (pcq, 1BH$_t$), 2.13 (s, 30H, Cp*), −6.66 (br, 2W−H−B), −7.42 (br, 2W−H−B); ^{13}C NMR (C$_6$D$_6$, 22 °C): δ 106.64 (s, η^5-C$_5$Me$_5$), 12.16 (s, CH$_3$ in η^5-C$_5$Me$_5$); IR (hexane, cm^{-1}): 2496w, 2467w (B−H$_t$).

X-ray Structure Determination. Suitable X-ray quality crystals of **3**, **4**, and **7** 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 **3** and **7** were collected and integrated using Oxford Diffraction Xcalibur-S CCD system and for **4** using Bruker AXS (Kappa Apex II) 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 and refined using SHELXL-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 3. Formula, C$_{20}$H$_{38}$B$_5$ClW$_2$; Crystal system, space group: triclinic, *P*1. Unit cell dimensions, a = 8.7448(4) Å, α = 100.489(4)°; b = 9.5666(6) Å, β = 95.436(4)°; c = 15.0780(6) Å, γ = 98.750(4)°; Z = 2. Density (calculated) 2.006 Mg/m^3. Final *R* indices [I > 2sigma(I)] R1 = 0.0242, wR2 = 0.0553. Index ranges $-10 \le h \le 10$, $-11 \le k \le 11$, $-17 \le l \le 17$. Crystal size 0.34 × 0.29 × 0.28 mm^3. Reflections collected 10618, independent reflections 4294, [*R*(int) = 0.0247], Goodness-of-fit on F^2 1.026.

Crystal data for 4. Formula, C$_{20}$H$_{37}$B$_5$Cl$_2$W$_2$; Crystal system, space group: orthorhombic, *Pbca*. Unit cell dimensions, a = 16.3283(5) Å, α = 90°; b = 14.5755(5) Å, β = 90°; c = 21.4963(6) Å, γ = 90°; Z = 8. Density (calculated) 1.997 Mg/m^3. Final *R* indices [I > 2sigma(I)] R1 = 0.0324, wR2 = 0.0697. Index ranges $-21 \le h \le 12$, $-16 \le k \le 19$, $-28 \le l \le 27$. Crystal size 0.38 × 0.32 × 0.30 mm^3. Reflections collected 19837, independent reflections 6290, [*R*(int) = 0.0280], Goodness-of-fit on F^2 1.043.

Crystal data for 7. Formula, C$_{20}$H$_{37}$B$_5$Cl$_2$W$_2$; Crystal system, space group: triclinic, *P*1. Unit cell dimensions, a = 8.8726(8) Å, α = 99.239(4)°; b = 9.6329(5) Å, β = 97.424(6)°; c = 15.0677(8) Å, γ = 99.257(6)°; Z = 2. Density (calculated) 2.060 Mg/m^3. Final *R* indices [I > 2sigma(I)] R1 = 0.0249, wR2 = 0.0594. Index ranges $-10 \le h \le 10$, $-11 \le k \le 11$, $-17 \le l \le 17$. Crystal size 0.28 × 0.26 × 0.21 mm^3. Reflections collected 10981, independent reflections 4321, [*R*(int) = 0.0206], Goodness-of-fit on F^2 1.086.

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Supporting Information Available: CIF Files for **3**, **4**, and **7**, as well as Cartesian coordinates of the DFT optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.