Synthesis and Characterization of Bicapped Hexagonal Bipyramidal 2,3-Cl_2-1,8-$\{Cp^*Re\}_2B_6H_4$ [$\{Cp^*Re\}_2\{\mu$-η^6:η^6-1,2-$B_6H_4Cl_2\}$, Cp* = η^5-C_5Me_5]: The Missing Link Connecting (p − 2) Skeletal Electron Pair Hypoelectronic Rhenaboranes and 24-Valence Electron Triple-Decker Complexes

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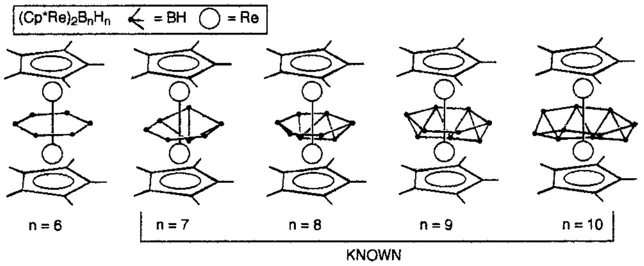
Metallaboranes of the earlier transition metals present interesting challenges to the well-established cluster electron-counting rules.[1−5] We have recently described a series of rhenaboranes of both unusual shape and electron count (Chart 1: rhenium−boron bonding not shown).[6,7] These boron-rich clusters, with formal skeletal electron counts (sep) considerably less than that prescribed, do not utilize the capping mechanism adopted by metal clusters and metal-rich metallaboranes to accommodate the electron-poor metal fragments. Rather, the structure taken up is one that retains the same total vertex connectivity as the most spherical forms found for the boranes but with a less uniform distribution of vertex connectivites.[8] Two vertices of high connectivity are occupied by the metal atoms, but the structures lack the three-connect vertices found in the capped structures exhibited by metal clusters.[8]

A proposed rationale for the observed electron counts of the closed rhenaboranes, $\{Cp^*Re\}_2B_nH_n$, $n = 7−10$, Cp* = η^5-C_5Me_5, is based on the hypothetical parent of the series, $\{Cp^*Re\}_2B_6H_6$. The latter is a closed, deltahedral, hypoelectronic rhenaborane with a (p − 2) sep count, but it is also a 24-valence electron (ve) triple-decker complex. Triple-decker complexes of this type are known for valence electron counts of 24−34 and, most importantly, the connection between composition, structural parameters, and electron count is well understood.[9−11] In essence, as the electron count decreases, the metal fragments move together, and the molecular orbital manifold responds accordingly. Two filled metal-localized orbitals, which are MM bonding and antibonding, respectively, separate with the latter rising to higher energy. At lower electron counts, a degenerate set of filled central ring orbitals, which are antibonding with respect to metal δ symmetry orbitals, also rise to higher energy as the M−M distance decreases. In the 24 ve triple-decker complex, the MM antibonding orbital and the M-ring antibonding orbitals are empty.[12−15]

Chart 1



As $\{Cp^*Re\}_2B_6H_6$ is the key compound in understanding these (p − 2) sep rhenaboranes, we sought to establish its existence and now report a dichloro derivative.

Although the reaction of $\{Cp^*ReH_2\}_2B_4H_4$ with BH_3•THF probably produces $\{Cp^*Re\}_2B_6H_6$, its spectroscopic simplicity and our inability to isolate the compound led us to seek an alternative approach. $BHCl_2$•SMe_2 is a monoborane we have used as an effective replacement of BH_3•THF twice previously;[16,17] thus, we explored its reactivity with $\{Cp^*ReH_2\}_2B_4H_4$. Despite the fact that H/Cl-exchange processes generate a complex product mixture, this approach was successful.[18] The molecular mass gives a molecular formula $\{Cp^*Re\}_2B_6H_4Cl_2$ corresponding to a dichloro-derivative of the desired compound. The ^{11}B NMR shows three types of boron environments in a 1:1:1 ratio, suggesting two types of BH and one BCl. The ^1H NMR reveals equivalent Cp* ligands and no metal hydrides or bridging hydrogen atoms. These data were consistent with a triple-decker complex with either a planar or puckered centrosymmetric B_6 ring and definitive structural characterization required a solid-state structure determination.

The molecular structure of **1** is shown in Figure 1 where it is seen to be $\{Cp^*Re\}_2\{\mu$-η^6:η^6-1,2-$B_6H_4Cl_2\}$ fully consistent with the solution spectroscopic data.[19] The molecule possesses a planar (mean plane standard deviation = 0.008 Å) 1,2-$B_6H_4Cl_2$ ring sandwiched between two Cp*Re fragments. The average Re−Re distance of 2.6889(5) Å is shorter than that found in $\{Cp^*Re\}_2B_nH_n$, $n = 7−10$, (av = 2.82 Å) but still longer than that expected for a Re−Re double bond.[7,20] The B−B and Re−B distances are in the range found for the other rhenaboranes

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(18) Reaction of excess $BHCl_2$•SMe_2 with $\{Cp^*ReH_2\}_2B_4H_4$ in toluene followed by heating at 75 °C for 18 h yielded a mixture of products from which four compounds could be isolated by fractional crystallization followed by TLC (silica gel with hexane/CH_2Cl_2, 7:3). Two were of known structure: $\{Cp^*Re\}_2B_7H_7$ and its monochloro derivative $\{Cp^*Re\}_2B_7H_6Cl$. The third, $\{Cp^*ReH\}_2B_5Cl_5$, is a new compound and will be described in the full publication. The fourth, $\{Cp^*Re\}_2\{\mu$-η^6:η^6-1,2-$B_6H_4Cl_2\}$, **1**, was isolated (second TLC band) in 4% yield as a yellow solid and crystalized by slow diffusion (CH_2Cl_2/ hexanes) at 5 °C. Spectroscopic data for **1**. MS(FAB-NBA), p^+ isotope cluster, 782 max, 6B, 2Re, 2Cl; ^{11}B NMR (C_6D_6, 22 °C, δ ppm, J Hz) 87.3 (s, 2B), 67.9 (d, 158, 2B), 59.3 (d, 161, 2B); ^1H NMR (C_6D_6, 22 °C, δ ppm) 7.7 (br q, 2H), 6.4 (br q, 2H), 1.96 (s, 30H)

(19) Crystal data: (170 K) $C_{20}H_{34}B_6Cl_2Re_2$, MW = 782.63, triclinic, *P*-1, $a = 10.511(1)$ Å, $b = 14.379(1)$ Å, $c = 16.776(2)$ Å, $\alpha = 89.965(2)°$, $\beta = 89.905(2)°$, $\gamma = 85.253(2)°$, $Z = 4$, $V = 2526.7(4)$ Å^3, $\mu = 9.79$ mm^{-1}, 11489 unique reflections, R1 = 0.0365 (0.0421 for all data), wR2 = 0.0794 (0.0872 for all data). Although the unit cell refined as nearly monoclinic, systematic absences were not consistent with monoclinic space groups. Therefore, the space group was determined to be *P*-1 with pseudomerohedral twinning (matrix applied: −1 0 0 0 −1 0 0 0 1), resulting in two molecules per asymmetric unit. The two components of the twin were determined to be present in a 76 to 24% ratio.

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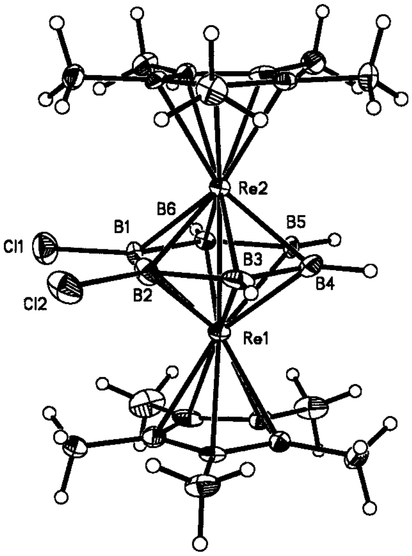
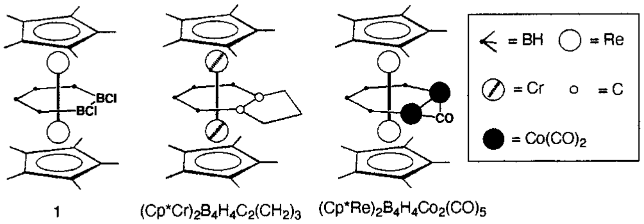


Figure 1. The molecular structure of $\{Cp^*Re\}_2\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}1,2\text{-}B_6H_4Cl_2\}$, **1**. Selected bond distances (Å) from one independent molecule: Re(1)−B(2) 2.145(12), Re(1)−B(1) 2.169(10), Re(1)−B(4) 2.192(11), Re(1)−B(5) 2.200(11), Re(1)−B(6) 2.229(10), Re(1)−B(3) 2.246(13), Re(1)−Re(2) 2.6887(5), Re(2)−B(2) 2.153(12), Re(2)−B(5) 2.161(10), Re(2)−B(4) 2.169(11), Re(2)−B(1) 2.173(10), Re(2)−B(6) 2.179(10), Re(2)−B(3) 2.231(12), Cl(1)−B(1) 1.746(10), Cl(2)−B(2) 1.787(12), B(1)−B(6) 1.710(15), B(1)−B(2) 1.780(16), B(2)−B(3) 1.700(18), B(3)−B(4) 1.732(19), B(4)−B(5) 1.701(17), B(5)−B(6) 1.732(15).

characterized. The former range from 1.70 to 1.78 Å and the average is about 0.3 Å longer than the average C−C distance in, for example, 26 ve $\{Cp^*V\}_2\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6\}$ (1.44 Å) with no V−V bond.[21] The methyl groups of the Cp* ligand are staggered relative to the chlorine atoms of the central ring forcing the antipodal BH hydrogens to near eclipsed orientations relative to methyl groups: however, the Cp* rings are nearly coplanar (dihedral angle 1.2°). The B_6 ring of **1** is not puckered as found in 24 ve $\{Cp^*V\}_2\{\mu\text{-}\eta^3\text{:}\eta^3\text{-}P_6\}$.[22] The rationale presented for the puckered structure has been detailed by others[13] and resides in the magnitude of the difference between the metal and bridging-ring orbital energies. The greater compatibility of boron and rhenium orbital energies favors a planar central ring normally associated with triple-decker complexes.

Chart 2



Compound **1** is isolobal with known 24 ve $\{Cp^*Cr\}_2\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$, Cp* = $\eta^5\text{-}C_5Me_5$,[23] and $\{Cp^*Re\}_2\text{-}\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}1,2\text{-}B_4H_4Co_2(CO)_5\}$[24] both of which contain planar, hexahapto, six-membered rings bridging two Cp*M fragments (Chart 2). **1**, however, is the first triple-decker complex with a six-membered central ring composed solely of boron atoms. In the context of the $\{Cp^*Re\}_2B_nH_n$ series (Chart 1), it is also a compound with (p − 2) sep, that is, the expected count for closo **1** is 9 sep which corresponds to a triple-decker complex of 30 ve. This dual identity provides justification for viewing the higher members of the $\{Cp^*Re\}_2B_nH_n$ series as triple-decker complexes with elaborated borane rings. Indeed, we have already shown that an analogous emptying of three MOs occurs when $\{Cp^*Re\}_2B_7H_7$ in a hypothetical tricapped trigonal prismatic geometry rearranges to the observed geometry—one is M−M antibonding and the other two are M_2-ring antibonding but with some B−B bonding character.[25] In essence, closed, dimetal metallaboranes of the earlier transition metals support oblate shapes possessing an equatorial borane belt, high-coordinate metal fragments in polar positions, and cross-cluster metal−metal bonding. A more detailed analysis is in progress.

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Supporting Information Available: CIF file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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