Chapter 1

PERFUNCTIONALIZED DODECABORATE CLUSTERS

This chapter provides a historical overview of dodecaborate clusters and summarizes research conducted over the past 70 years. Emphasis is on discussions around the electronic structure and stability of dodecaborates, as well as recent developments toward hypoelectronic perfunctionalized dodecaborates and their applications.

A range of theoretical and experimental studies followed Lipscomb's initial structural characterization of the closo-dodecaborate dianion (closo-$[B_{12}H_{12}]^{2-}$*) in 1960. These included the synthesis of a range of partially substituted closo-dodecaborates, as well as the persubstituted closo-dodecahalo-dodecaborates (*$[B_{12}X_{12}]^{2-}$*; X = F, Cl, Br, I). Up until the late 1990s, it was assumed that stable electronic configurations were reserved for closed-shell dianionic closo-dodecaborates. However, pioneering work conducted in the Hawthorne lab demonstrated that the alkyloxy- and aryloxy-perfunctionalized closo-*$[B_{12}(OR)_{12}]^{2-}$ *clusters could undergo two reversible single-electron oxidations to yield hypocloso-*$[B_{12}(OR)_{12}]^{1-}$ *and hypercloso-*$B_{12}(OR)_{12}$ *species. Following work by the Spokoyny lab and others have shown a range of promising applications for hypercloso-*$B_{12}(OR)_{12}$ *clusters, including their use as photoredox reagents, in charge-storage devices and as dopants in conducting polymers.*

1.1 Dodecaborate Clusters

The early 1950s saw an increasing interest in systematic investigation of boron hydrides and rationalization of their stability and bonding patterns. In 1954, Lipscomb and co-workers introduced the "three-center bond" concept.[1] They argued that a three-center bond description of electron-deficient boron hydrides may be more appropriate than previously suggested resonance based structures. Using the three-center bond approach, Lipscomb explored the binding patterns of a number of known boron hydrides: B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} and $B_{10}H_{14}$. Additionally, several at the time unknown structures were explored—including B_6H_6 and the icosahedral $B_{12}H_{12}$ dodecaborate. Linear combination of atomic orbitals (LCAO) calculations for B_6H_6 indicate a triply degenerate highest occupied molecular orbital (HOMO), partially filled with four electrons. Due to its unfilled B-B bonding HOMO, B_6H_6 is predicted to be unstable. The relative orbital energies of $B_{12}H_{12}$ were not obtained due the complexity of performing the required LCAO calculations. Lipscomb argued that the HOMO of $B_{12}H_{12}$ might be three-fold or four-fold degenerate—where the former would lead to a stable closed-shell configuration, while the latter would likely lead to an unstable open-shell species.

Following the theoretical investigations by Lipscomb, Longuet-Higgins and Roberts used more in-depth molecular orbital calculations to explore the stability of boron hydrides.[2] Based on the relative ordering of the B-B bonding orbitals, they reported that $B_{12}H_{12}$ would likely not be stable. However, their predictions indicated that a dianionic closed-shell $[B_{12}H_{12}]^{2-}$ species might exist. $B_{12}H_{12}$ has forty-eight valence electrons, of which twenty-four are localized to twelve two-center B-H bonds. This leaves twenty-four electrons for B-B bonding. Assuming near-icosahedral symmetry, Longuet-Higgins predicted thirteen B-B bonding orbitals, where the four highest energy orbitals create a four-fold degenerate g_u set. As postulated by Lipscomb, this leads to the conclusions that icosahedral $B_{12}H_{12}$ should not be stable, as the four-fold degenerate g_u would lead to a partially unfilled HOMO. However, a dianionic $[B_{12}H_{12}]^{2-}$ species may be stable as the two extra electrons would result in a fully occupied HOMO.

The first mention of experimentally observed $B_{12}H_{12}$ came from Shapiro and Williams.[3] Reacting diborane (B_2H_6) with decaborane ($B_{10}H_{14}$) at elevated temperatures resulted in the formation of a light yellow solid. The final product appeared to be a polymerized borane. However, based on gasometrical analysis the authors proposed that the initial product of the reaction was $B_{12}H_{12}$. In 1960 Pitochelli and Hawthorn confirmed Longuet-Higgins and Lipscombs predictions by isolating the icosahedral $[B_{12}H_{12}]^{2-}$ dodecaborate (henceforth referred to as *closo*-dodecaborate or *closo*-$[B_{12}H_{12}]^{2-}$), although in very low yield (3.8%).[4] Later that year, Lipscomb reported an X-ray diffraction study showing that the structure of *closo*-dodecaborate possessed near-icosahedral symmetry (Figure 1.1).[5] Spectroscopic investigations by Muetterties and co-workers followed soon thereafter.[6] Hoffmann and Lipscomb used the newly obtained experimental data to guide refinement of LCAO calculations. Their work confirmed Longuet-Higgins overall qualitative description of *closo*-dodecaborate and provided additional quantitative information, including a ~14 eV calculated band gap.[7,8] A calculated electronic structure for *closo*-dodecaborate by Bambakidis and Wagner is shown in Figure 1.2.[9]

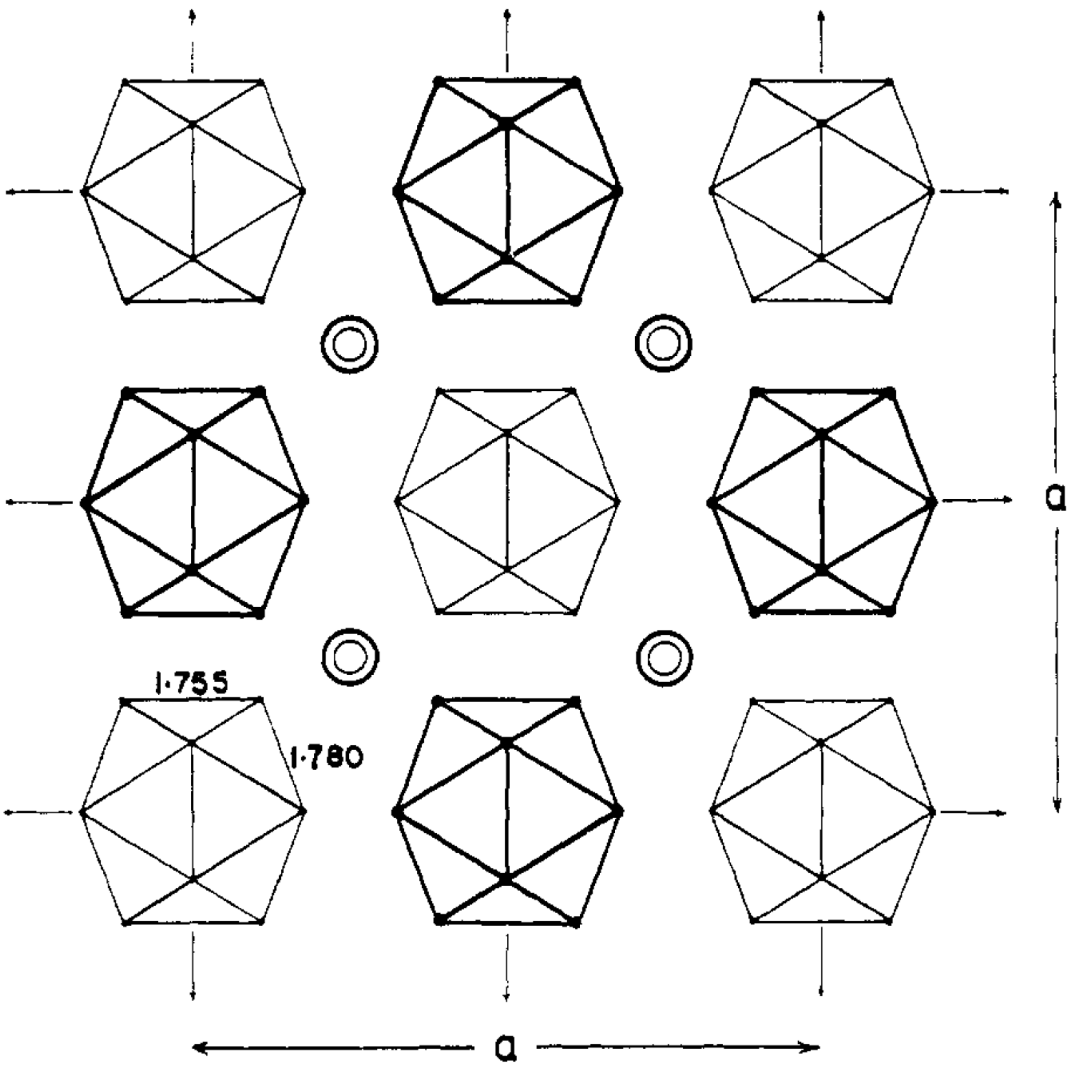


Figure 1.1. Crystallographic data reported by Lipscomb demonstrating the near-icosahedral symmetry of *closo*-$[B_{12}H_{12}]^{2-}$. Reprinted with permission from Wunderlich, J. A.; Lipscomb, W. N. STRUCTURE OF B12H12-2 ION. *J. Am. Chem. Soc.* **1960**, *82* (16), 4427–4428. Copyright (1960) American Chemical Society.

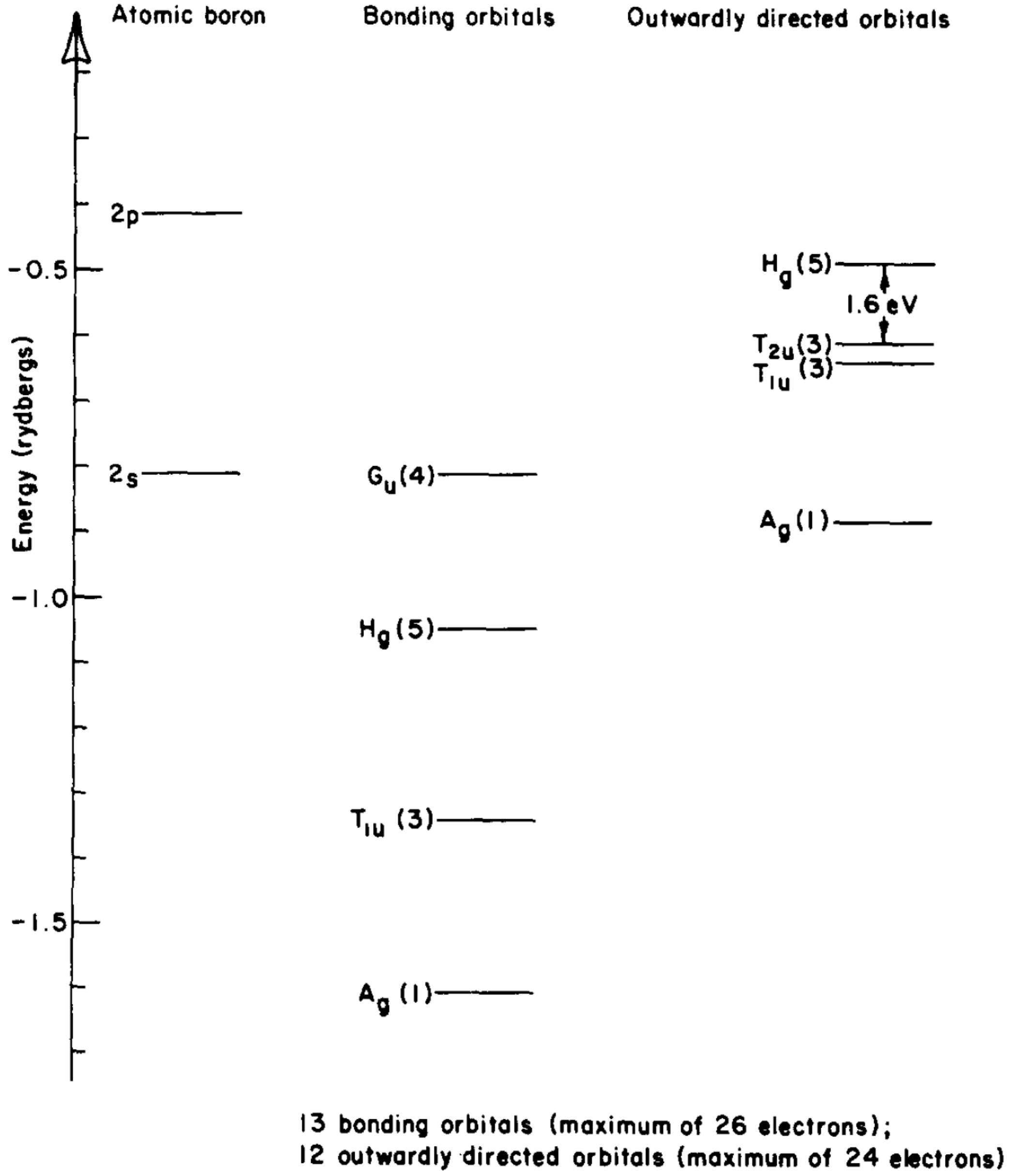


Figure 1.2. Electronic structure of *closo*-$[B_{12}H_{12}]^{2-}$ calculated by Bambakidis and Wagner. Reprinted from Bambakidis, G.; Wagner, R. P. Electronic Structure and Binding Energy of the Icosahedral Boron Cluster B12. *Journal of Physics and Chemistry of Solids* **1981**, *42* (11), 1023–1025. Copyright (1981), with permission from Elsevier.

The interest in dodecaborates was further enhanced by the discovery of more convenient methods for synthesizing *closo*-$[B_{12}H_{12}]^{2-}$ salts. Two classes of high-yield reactions were reported, both relying on reacting diborane with a base in a pressurized reactor. In the first route (eq. 1) sodium borohydride is reacted with diborane in a basic solvent, typically triethylamine. The second route (eq. 2) involves reacting an alkylamine or a borane-alkylamine complex with diborane. Reactions yields of > 90% are readily achieved using optimized variations of these reactions.[10–12] Modern synthetic schemes replace diborane with larger boranes, commonly $B_{10}H_{14}$, which avoids the hazardous pressurized conditions required for the early synthetic pathways. Today, a wide range of synthetic methods have been reported and dozens of *closo*-$[B_{12}H_{12}]^{2-}$ salts have been prepared; including metal, ammonium, trimethylsulfonium, tetraphenylphosphonium and guanidinium salts.[13]

$$2NaBH_4 + 5B_2H_6 \rightarrow Na_2[B_{12}H_{12}] + 13H_2 \qquad (1)$$

$$2R_3N + 6\mathrm{B}_2H_6 \rightarrow [R_3NH]_2[B_{12}H_{12}] + 11H_2 \qquad (2)$$

As expected from the theoretical investigations discussed above, attempts to isolate oxidized forms of *closo*-$[B_{12}H_{12}]^{2-}$ have proved unsuccessful. Specifically, Wiersema and Middaugh demonstrated that one-electron electrochemical oxidation of *closo*-dodecaborate leads to irreversible formation of $[B_{24}H_{23}]^{3-}$. This species likely corresponds to the hydrogen-bridged dimer 1,1'-μ-hydro-bis(undecahydro-*closo*-dodecaborate)(3-).[14]

The 1970s saw further generalization of the theoretical framework for rationalizing structures and stability trends of electron-deficient polyhedral clusters. A landmark paper by Wade presented a set of principles for predicting the structure of cluster compounds by counting the number of vertices and the number of skeletal bonding orbitals. These guidelines, which have become known as "Wade's rule", state that the number of skeletal bonding pairs of stable *closo* (*n*-vertex), *nido* ((*n* - 1)-vertex) and *arachno* ((*n* - 2)-vertex) clusters must be (*n* + 1). Wade's rule has been successfully applied to rationalize the structure of a wide variety of polyhedral cluster compounds.[15,16]

Models considering three-dimensional aromaticity also provided important insights toward understanding the stability of polyhedral boranes. Early theoretical work by Aihara showed that the resonance model could be extended into three dimensions using three-center bonding. Through this approach, resonance stabilization can be used to explain the stability of various boron polyhedra. The three-dimensional aromaticity of polyhedral boron compounds has gained additional support through later computational studies and is thought to be an important contributor to the inert nature of *closo*-dodecaborate.[17,18]

1.2 Functionalization of *closo*-Dodecaborate

A range of studies on the reactivity and physical properties of *closo*-dodecaborate were published in the decade following its initial isolation by Pitochelli and Hawthorn. Muetterties and co-workers performed several experimental studies on functionalization of *closo*-dodecaborate.[19,20] *Closo*-dodecaborate is exceptionally stable toward strong bases, strong acids and oxidizing agents. The cluster remains intact even in hot sodium hydroxide and sodium methoxide solutions. In fact, *closo*-dodecaborate can be converted into stable $(H_3O)_2[B_{12}H_{12}]\bullet x(H_2O)$ by reaction with strong acids, without compromising the integrity of the cluster. The stability toward acid is noteworthy, as most boron hydrides rapidly decompose under acidic conditions.

Closo-dodecaborate is susceptible to electrophilic substitution, where hydrogen atoms are replaced by an electrophilic reagent. *Closo*-$[B_{12}H_{12}]^{2-}$ can be reacted with halogens (X = F, Cl, Br, I) to yield fully substituted *closo*-$[B_{12}X_{12}]^{2-}$. Partially substituted haloborates ($[B_{12}X_nH_{12-n}]^{2-}$, n<12) can be prepared through similar procedures. However, the rapid reaction rates makes isolating species with a low degree of halogen substitution challenging, in particular for the smaller halogens (F, Cl). Certain partially substituted haloborates can be prepared using elemental halogens, like iodine monochloride and N-bromosuccinimide, or hydrogen fluoride in the case of fluoroborates. Additional reactivity can be afforded by using the acid derivative, $(H_3O)_2[B_{12}H_{12}]\bullet x(H_2O)$. For example, reacting these acidic clusters with alcohols or carboxylic acids yield $[B_{12}H_{11}(OH)]^{2-}$ and $[B_{12}H_{12-n}(OR)_n]^{2-}$ (n = 1, 2).[19–21]

Development of *closo*-dodecaborate derivatives has continued to be an active field of research. Many monosubstituted and disubstituted variants have been reported, including clusters carrying boron-carbon bonds, boron-nitrogen bonds, boron-oxygen bonds, boron-sulfur bonds, as well as boron-phosphorus and boron-arsenic bonds. Some interesting examples include carbonyl derivatives, amines, amides, alkyl and aryl derivatives. Notably, clusters carrying mercapto-functionalities have received much attention due to their potential applications in boron neutron capture therapy.[22]

This thesis is primarily concerned with persubstituted derivates of *closo*-dodecaborate. Up until the late 1990s the only examples of perfunctionalized dodecaborates were the dodecahalo-*closo*-dodecaborates discussed above. The first example of a non-halogen perfunctionalized dodecaborate came from Krebs and co-workers in 1997, who reported the selenoboratoborate *closo*-$[B_{12}(BSe_3)_6]^{8-}$, where the hydrogens had been substituted by six bidentate BSe_3 groups.[23] A year later, Hawthorne reported a permethylated *closo*-$[B_{12}Me_{12}]^{2-}$ cluster (Me = CH_3).[24,25]

A key breakthrough came in 1999 when Hawthorne and co-workers reported the isolation of dodecahydroxy-*closo*-dodecaborate (*closo*-$[B_{12}(OH)_{12}]^{2-}$).[26] The synthesis of *closo*-$[B_{12}(OH)_{12}]^{2-}$ is performed by refluxing $Cs_2[B_{12}H_{12}]$ in 30% hydrogen peroxide for several days and produces good to excellent yields (65-90%).[27] To mitigate risks involved with using concentrated hydrogen peroxide at elevated temperatures, the $Cs_2[B_{12}H_{12}]$ starting material must be rigorously purified before attempting the reactions. Researchers are advised to exercise caution when trying this synthesis as minor organic impurities may cause explosive mixtures. That said, this synthetic pathway is still used and has proven remarkably robust—provided appropriate safety measures are taken.[27,28] Following the isolation of dodecahydroxy-*closo*-dodecaborate, the Hawthorn group demonstrated that these clusters could be reacted with benzyl chloride to form $[B_{12}(OBz)_{12}]^{2-}$ (Bz = $CH_2C_6H_5$). Using the reaction pathways shown in Figure 1.3, the reactivity was expanded to a range of ether and ester derivatives of *closo*-$[B_{12}(OH)_{12}]^{2-}$. Table 1.1 shows examples of the ether derivatives published by the Hawthorne group.

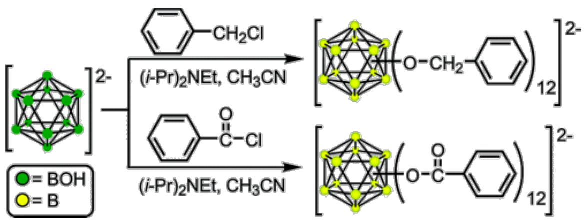


Figure 1.3. Synthetic method for perfunctionalized ether and ester derivatives of *closo*-$[B_{12}(OH)_{12}]^{2-}$ developed by Hawthorne and co-workers. An acetonitrile solution of *closo*-$[B_{12}(OH)_{12}]^{2-}$ and the relevant reactant is refluxed in the presence of base, yielding the desired *closo*-$[B_{12}(OR)_{12}]^{2-}$ cluster. Reprinted with permission from Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. Synthesis of Stable Dodecaalkoxy Derivatives of Hypercloso-B12H12. *J. Am. Chem. Soc.* **2005**, *127* (51), 18243–18251. Copyright (2005) American Chemical Society.

Table 1.1. Examples of *closo*-$[B_{12}(OR)_{12}]^{2-}$ clusters developed by the Hawthrone lab. Method 1 refers to refluxing $[B_{12}(OH)_{12}]^{2-}$ with the appropriate alkyl or aryl halide and *N,N'*-diisopropylamine in acetonitrile. Method 2 involves performing the same reaction under mild argon pressure in an autoclave to achieve elevated temperature and reduced reaction times. Reprinted with permission from Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. Synthesis of Stable Dodecaalkoxy Derivatives of Hypercloso-B12H12. *J. Am. Chem. Soc.* **2005**, *127* (51), 18243–18251. Copyright (2005) American Chemical Society.

closomer ether	R in $(BOR)_{12}$	method/ reagent[a]	reaction time/ temp	yield[b] (%)
2	benzyl	1/benzyl bromide	6 d/reflux	69
		2/benzyl chloride	4 h/150 °C	65
3	ethyl	2/bromoethane	12 h/150 °C	70
4	hexyl	1/1-bromohexane	23 d/reflux	80
		2/1-bromohexane	8 h/150 °C	75
		2/*n*-hexyl tosylate	2 h/150 °C	70
5	pentyl	1/1-bromopentane	21 d/reflux	78
		2/1-bromopentane	7 h/150 °C	75
6	allyl	1/allyl bromide	7 d/reflux	55
		2/allyl chloride	3 h /150 °C	60
7	3-butenyl	1/4-bromo-1-butene	19 d/reflux	65
		2/4-bromo-1-butene	6 h/150 °C	62
8	3-methyl-1-butyl	2/1-(bromomethyl)butane	8 h /150 °C	75
9	4-fluorobenzyl	1/4-fluorobenzyl bromide	5 d/reflux	59
		2/4-fluorobenzyl chloride	1 h/150 °C	68
10	methyl	2/methyl tosylate	2 h/150 °C	50
11	3-fluorobenzyl	2/3-fluorobenzyl chloride	4 h/150 °C	60
12	4-chlorobenzyl	2/4-chlorobenzyl chloride	5 h/150 °C	75
13	4-bromobenzyl	2/4-bromobenzyl bromide	5 h/150 °C	70
14	3-bromobenzyl	2/3-bromobenzyl bromide	5 h/150 °C	65
15	4-methylbenzyl	2/4-methylbenzyl chloride	5 h/150 °C	55
16	4-methoxybenzyl	2/4-methoxybenzyl chloride	1 h/150 °C	30

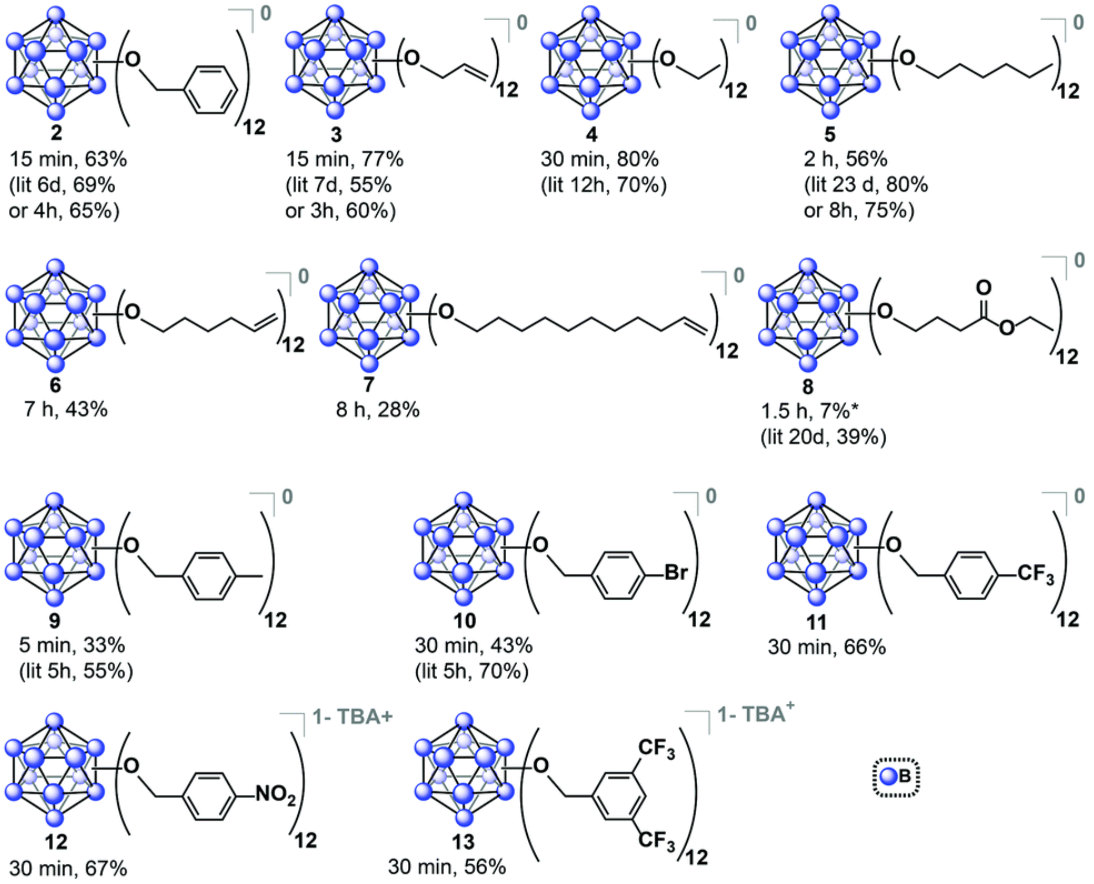
[a] Acetonitrile was used in all reactions. [b] Isolated yield of $B_{12}(OR)_{12}$ based on $(TBA)_2$-**1**.

1.3 Hypoelectronic Dodecaborates

The first example of a stable hypoelectronic dodecaborate derivative came when the Hawthorne group reported the isolation a stable salt of the singly oxidized $[B_{12}Me_{12}]^{1-}$ cluster.[30] Quickly thereafter, in conjunction with their publications on alkoxy-perfunctionalized clusters, the same group showed that $[B_{12}(OBz)_{12}]^{2-}$ could undergo reversible one-electron oxidations to yield open-shell anionic $[B_{12}(OBz)_{12}]^{1-}$ and neutral $B_{12}(OBz)_{12}$ species. These oxidized pseudo-icosahedral species have since become known as *hypocloso*-dodecaborates ($[B_{12}]^{1-}$ monoanion) and *hypercloso*-dodecaborates ($B_{12}{}^{0}$ neutral), to signify their deviation from Wade's rule.[31] Following publications demonstrated that the ability to form hypoelectronic *hypocloso*-$[B_{12}(OR)_{12}]^{1-}$ and *hypercloso*-$B_{12}(OR)_{12}$ states is a general feature of alkyloxy- and aryloxy-perfunctionalized dodecaborates.[29,32] Hypoelectronic states can also be isolated for perfunctionalized halide and hydroxyl derivatives of dodecaborate. Under certain conditions, synthesis of *closo*-$[B_{12}(OH)_{12}]^{2-}$ leads to formation of *hypocloso*-$[B_{12}(OH)_{12}]^{1-}$ as a side product, which can be isolated as the cesium salt $Cs[B_{12}(OH)_{12}]$.[33] The halide derivatives *closo*-$[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, I) undergo electrochemical single-electron oxidation to *hypocloso*-$[B_{12}X_{12}]^{1-}$ in liquid sulfur dioxide at highly oxidizing potentials (~1.7 V for X = F, ~2.1 V for X = Cl, ~2.3 V for X = Br; potentials referenced to the ferrocene-ferrocenium couple). In contrast to the reversible oxidations observed for $[B_{12}(OR)_{12}]$ clusters, the halide derivatives, at best, display pseudo-reversible redox events. The highest degree of reversibility is achieved when X = Cl or Br. In line with these results, *hypocloso*-$[B_{12}Cl_{12}]^{1-}$ and *hypocloso*-$[B_{12}Br_{12}]^{1-}$ can be chemically isolated through oxidation with arsenic pentafluoride in liquid sulfur dioxide.[34,35] *hypocloso*-$[B_{12}F_{12}]^{1-}$ is more challenging to generate chemically, however, a crystal structure of a cobaltocenium salt of *hypocloso*-$[B_{12}F_{12}]^{1-}$ has been reported.[36]

The next breakthrough came when the Spokoyny lab presented a convenient route for rapid generation of *hypercloso*-$B_{12}(OR)_{12}$ using microwave synthesis. Table 1.2 shows some of the clusters synthesized using this method and compares the reaction times to those reported for earlier methods. Reactions that used to take many hours, sometimes days, could now be achieved in a matter of minutes. Access to straightforward and scalable synthesis methods have facilitated systematic characterization and investigation into potential applications of $[B_{12}(OR)_{12}]$ clusters.

Table 1.2. *hypercloso*-$B_{12}(OR)_{12}$ clusters obtained through microwave synthesis. Previously reported reaction times and yields shown in parenthesis, when available. Reproduced from Ref. 27 with permission from The Royal Society of Chemistry.



The majority of the *hypercloso*-$B_{12}(OR)_{12}$ clusters reported are indefinitely stable under ambient conditions, which is remarkable considering that even single-electron oxidation leads to immediate decomposition of *closo*-$[B_{12}H_{12}]^{2-}$. Multiple factors contribute to stabilizing the B_{12}^{0} core in *hypercloso*-$B_{12}(OR)_{12}$. Electron donation from the R-groups modulates redox potentials and play an important role in increasing the electron density in B-B bonding orbitals. In line with this, the redox potential of $[B_{12}(OR)_{12}]$ clusters carrying aryl substituents can be systematically tuned based on the Hammett constant of the aryl groups, as demonstrated by the linear relationship between redox potentials and Hammett constants shown in Figure 1.4. Furthermore, upon oxidation the cluster is distorted, which lowers the overall energy and avoids energetically unfavorable open-shell configurations by breaking the icosahedral (I_h) symmetry. There has been some controversy around the nature of the distortion, however, most authors believe a $I_h \rightarrow D_{3d}$ transformation is involved in stabilizing oxidized $[B_{12}(OR)_{12}]$ clusters. This leads to a closed-shell *hypercloso*-$B_{12}(OR)_{12}$ $a_{1u}^{0}a_{2u}^{2}e_{u}^{4}$ configuration, avoiding the unstable open-shell g_u^{4} configuration predicted for $B_{12}H_{12}$. An important consequence of depopulation of the a_{1u} is the appearance of a strong visible absorption band (~ 455 nm $\varepsilon > 2*10^{4}$ $M^{-1}cm^{-1}$). The reversible redox behavior and visible absorption have opened up for applications in a range of fields, including photochemistry,[37,38] charge storage[39] and as dopants in conducting polymers.[40]

1.4 Applications of *hypercloso*-$B_{12}(OR)_{12}$

To date, the most widely explored applications of *hypercloso*-$B_{12}(OR)_{12}$ involve using the clusters as photoredox reagents, and in particular, their use as photoinitiators for cationic polymerization.

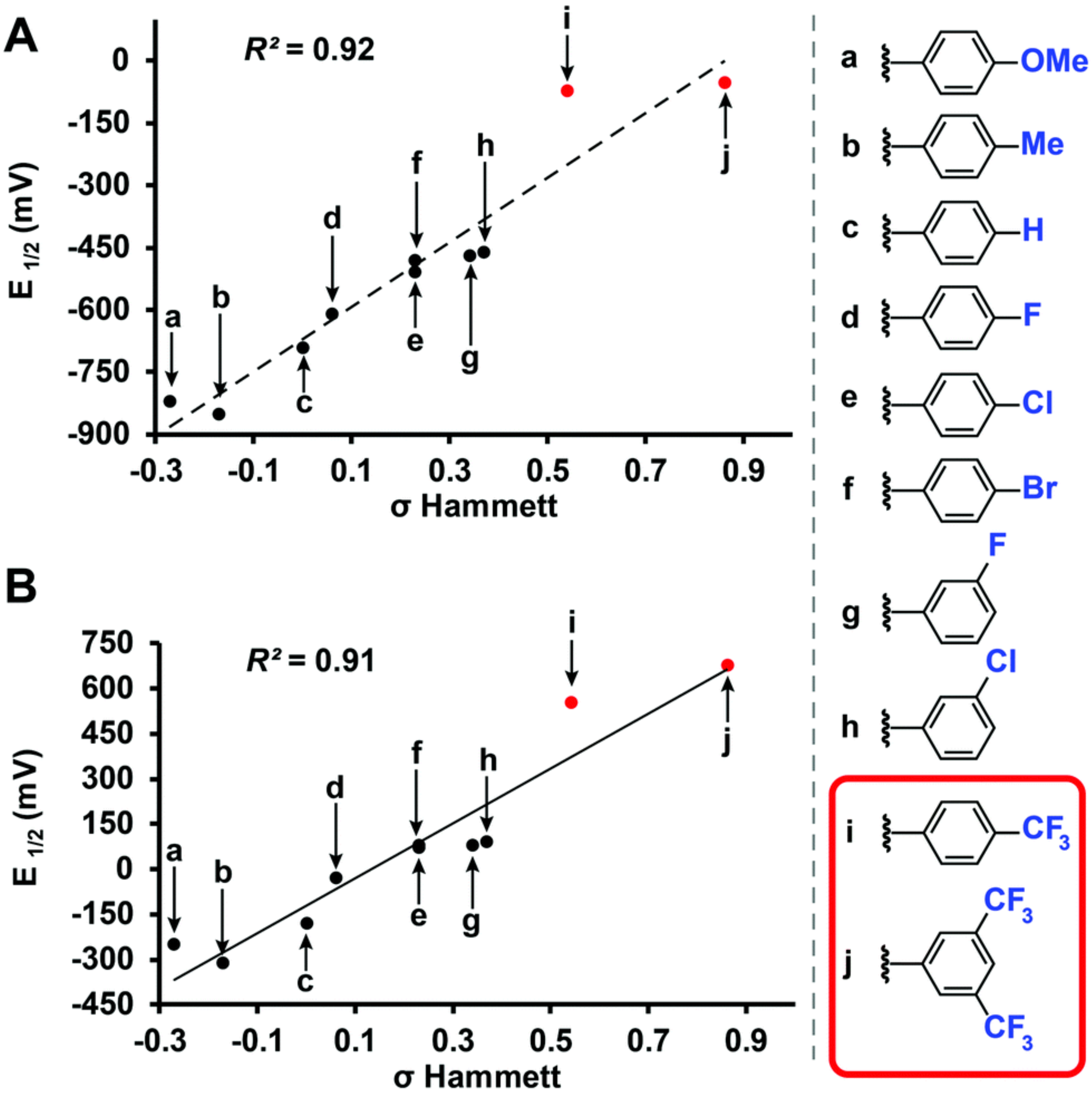


Figure 1.4 Relationship between $[B_{12}(OR)_{12}]$ redox potentials and substituent Hammett constants. Potentials are reported versus the ferrocene-ferrocenium couple. Reproduced from Ref. 27 with permission from The Royal Society of Chemistry.

The Spokoyny lab demonstrated polymerization of electron-rich styrenes using *hypercloso*-$B_{12}(OBz)_{12}$ as a photoinitiator. Using the more oxidizing perfluoro analogue, *hypercloso*-$B_{12}(OCH_2C_6F_5)_{12}$, they were able to expand the reactivity to less electron-rich styrenes. Remarkably, *hypercloso*-$B_{12}(OCH_2C_6F_5)_{12}$ is also able to photoinitiate polymerization of isobutylene, which had previously not been achieved in metal-free systems. Figure 1.5 shows a schematic of the photopolymerization reaction and the highly branched poly(isobutylene) product. Part of the work presented in this thesis aims to rationalize the photooxidative properties of *hypercloso*-$B_{12}(OR)_{12}$ clusters.[28,37]

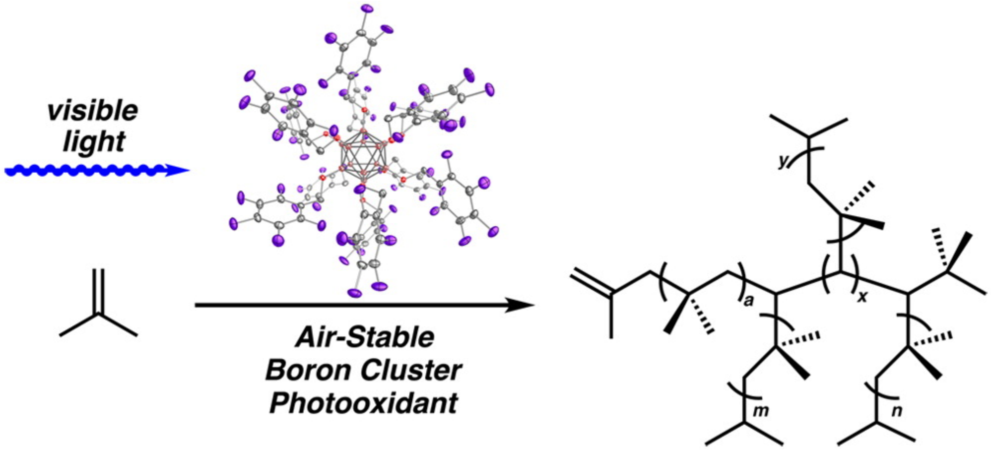


Figure 1.5. Photopolymerization of isobutylene using *hypercloso*-$B_{12}(OCH_2C_6F_5)_{12}$ results in a highly branched polymer. Reprinted with permission from Messina, M. S.; Axtell, J. C.; Wang, Y.; Chong, P.; Wixtrom, A. I.; Kirlikovali, K. O.; Upton, B. M.; Hunter, B. M.; Shafaat, O. S.; Khan, S. I.; et al. Visible-Light-Induced Olefin Activation Using 3D Aromatic Boron-Rich Cluster Photooxidants. *Journal of the American Chemical Society* **2016**, *138* (22), 6952–6955. Copyright (2016) American Chemical Society.

The highly reversible redox behavior of $[B_{12}(OR)_{12}]$ clusters have resulted in interesting applications as dopants in conducting polymers and in charge-storage devices. Recent work showed that P3HT (poly(3-hexylthiophene-2,5-diyl) films doped with the bulky dodecaborate *hypercloso*-$B_{12}(OCH_2\text{-}3,5\text{-}(CF_3)_2\text{-}C_6H_3)_{12}$ display conductivities roughly an order of magnitude higher than P3HT films prepared with the conventional dopant F_4TCNQ (2,3,5,6-tetrafluoro-tetracyanoquinodimethane). In these systems, introduction of the oxidizing *hypercloso*-B_{12}^{0} species produces a hole on the polymer and a negative charge confined to the B_{12} cluster core. The authors argue that the bulky 3,5-$(CF_3)_2$-C_6H_3 groups result in a highly shielded *hypocloso*-$[B_{12}]^{1-}$ core, which improves polymer hole conductivity.[40] Applications in redox flow batteries have also shown promising results. A single type of $[B_{12}(OR)_{12}]$ cluster can be used in both cell compartments, as shown in Figure 1.6, or the anodic and cathodic electrolytes can be prepared using clusters equipped with differing R-groups. The former utilizes the split between the $[B_{12}]^{1-/2-}$ couple and $[B_{12}]^{0/1-}$ couple to drive the voltage, while the latter uses the difference in redox potential provided by changing the R-group. Negligible cluster decomposition after > 1000 hours of battery cycling demonstrates the robustness of the $[B_{12}(OR)_{12}]^{0/1-/2-}$ redox system.

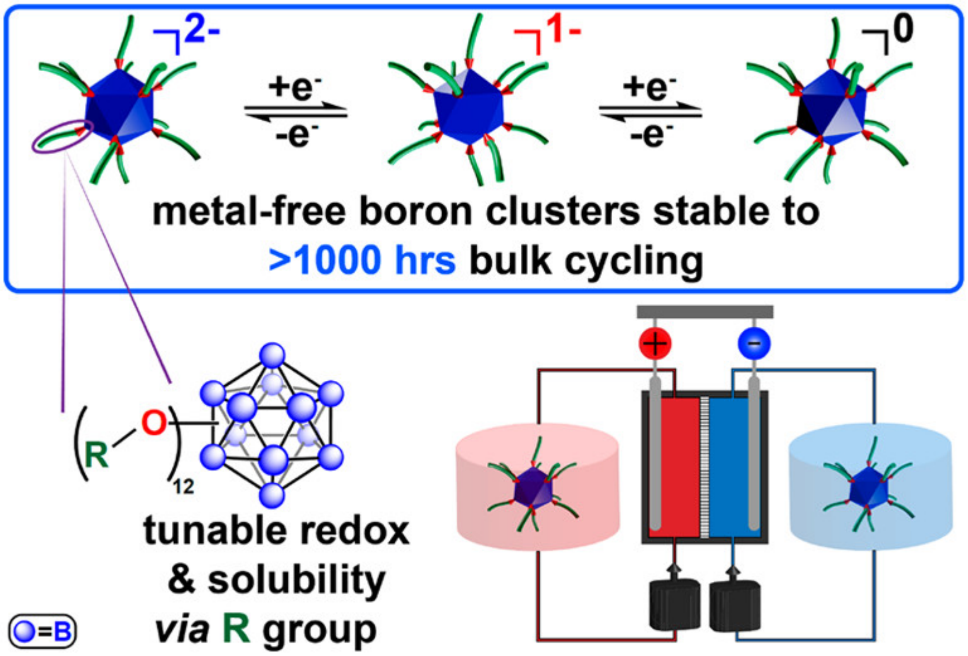


Figure 1.6. Schematic of a $[B_{12}(OR)_{12}]$ redox flow battery. The blue electrolyte contains $[B_{12}(OR)_{12}]^{2-}$, while the red electrolyte contains $B_{12}(OR)_{12}^{0}$. The battery voltage is obtained from the split between the $[B_{12}]^{1-/2-}$ and $[B_{12}]^{0/1-}$ redox couples. Reprinted with permission from Barton, J. L.; Wixtrom, A. I.; Kowalski, J. A.; Qian, E. A.; Jung, D.; Brushett, F. R.; Spokoyny, A. M. Perfunctionalized Dodecaborate Clusters as Stable Metal-Free Active Materials for Charge Storage. *ACS Appl. Energy Mater.* **2019**, *2* (7), 4907–4913. Copyright (2019) American Chemical Society.

1.5 Concluding Remarks

Dodecaborate clusters have been a lively field of research since the early 1950s. Several groundbreaking discoveries have been made over the past two decades, most notably, the isolation of alkyloxy-perfunctionalized dodecaborates and the discovery of hypoelectronic *hypocloso*-$[B_{12}(OR)_{12}]^{1-}$ and *hypercloso*-$B_{12}(OR)_{12}$ states. *hypercloso*-$B_{12}(OR)_{12}$ shows remarkable stability, considering the instability of oxidized $[B_{12}H_{12}]$ species and challenges associated with oxidizing dodecahalo-*closo*-dodecaborates. The tunability of the electrochemical properties, reversible redox behavior and strong visible absorption bands make *hypercloso*-$B_{12}(OR)_{12}$ clusters interesting for a range of applications. Recent reports include their use as photoredox reagents, as dopants in conducting polymers and in charge-storage devices. Understanding the electronic structure is key to rationalizing these properties. Regrettably, experimental evidence is currently lacking, and most electronic structure descriptions are based on often contradictory computational work. This thesis aims to address some of these issues using spectroscopic and electrochemical techniques.

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