

Polyhedral boron-containing cluster chemistry: Aspects of architecture beyond the icosahedron*

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Abstract: For the structural extent of the polyhedral molecular chemistry of boron to rival that of the organic chemistry of the carbon hydrides, (a) the individual boron-containing polyhedra need to be fused together to make larger contiguous covalent assemblies, and (b) an intermolecular chemistry needs to be developed. Contemporary examples are given that illustrate novel chemistry in both these areas and that may point the way to some future developments.

INTRODUCTION

Two elements, boron and carbon, have complex chemistries based on their hydrides. Nature and carbon have worked together for many millenia of millenia. One consequence of this is that an amazingly large structural variety of carbon hydride-based molecules is now known. There is, correspondingly, a very extensive molecule–molecule interaction chemistry, well exemplified by the exceedingly complex and subtle behavior of biological systems. Much of this incredible variety derives from larger molecules in which the basic carbon-hydride building blocks—rings, chains, etc.—are fused together architecturally to make much bigger molecules. The basic structural building blocks of the boron hydrides are polyhedral clusters, with a natural single-cluster size-limit of about 12 to 14 vertices. This limit is associated with the very high stability of the 12-vertex, 26-electron icosahedron. It is perhaps reasonable to say that the vast majority of the boron-hydride cluster chemistry of the previous century has been based on single molecules that are based on single boron-containing clusters. For the man-made chemistry of the boron hydrides to even start to approach the extent of carbon-hydride chemistry that nature has engendered, it is necessary to join, or to fuse, these single clusters together in a covalent manner to make larger assemblies that we might call “supermolecules”. To further match the extent of carbon-hydride chemistry, it is also necessary to explore and develop their molecule–molecule interaction chemistry—their “supramolecular” assembly behavior. Sometimes, these two aspects may merge as the larger molecules may have surface features that geometrically fit together very efficiently with their neighbors. Additionally, the larger molecules will have larger surfaces, for which the cumulative sum of the non-bonded interactive abilities of individual atoms approaches or exceeds binding energies associated with single covalent bonds. In this article, we take results from our laboratories in Leeds briefly to exemplify

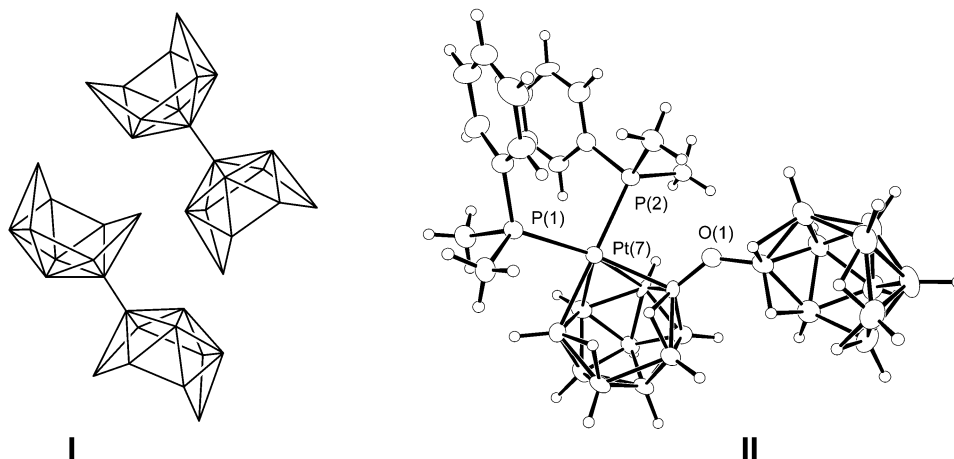
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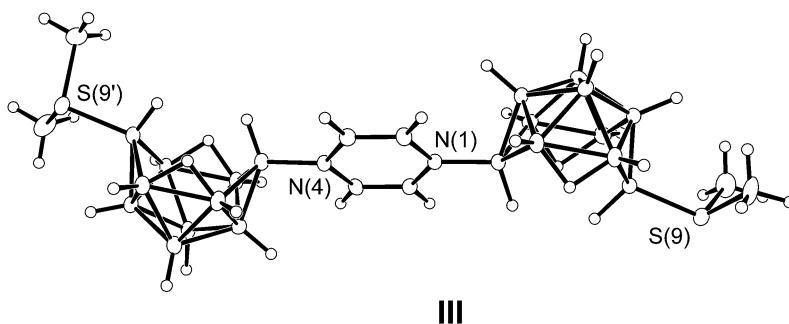
some of the developing architectural aspects of some of these supermolecular and supramolecular extensions of boron hydride chemistry beyond the single-cluster, single-molecule horizons associated with the structural barrier of the stable icosahedron.

SUPERMOLECULAR ASPECTS: COVALENT INTERCLUSTER INTERACTIONS

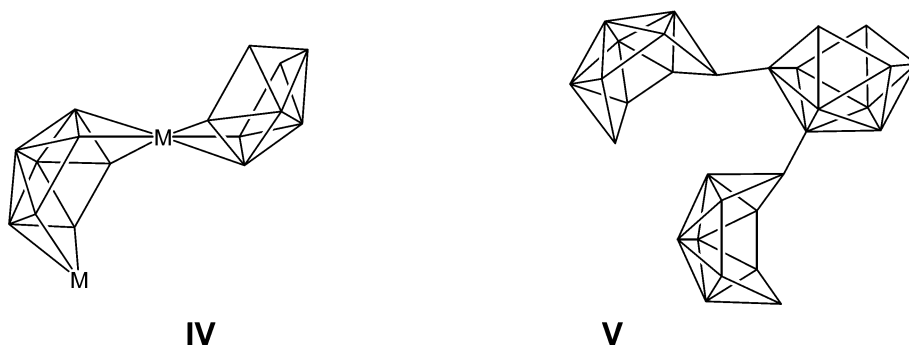
The simplest way of linking two clusters together is by a simple two-electron, two-center sigma link. This structural motif is well recognized, for example, in various isomers of bi(*nido*-decaboranyl), $[(B_{10}H_{13})_2]$ (Schematics **I**) (e.g., IUCr no. BR 1315) [1]. This type of linkage can be extended in two ways. One way is by the intercalation of a more extended linkage chain, for example, one atom as in $[(PMe_2Ph)_2PtB_{10}H_{11}]O\{B_{10}H_{13}\}$ **II** (CCDC 198875), or a more elaborate linkage as in $[(Me_2S)B_{10}H_{12}]NC_4H_4N\{B_{10}H_{12}(SMe_2)\}$ **III** (CCDC 18898) [2].



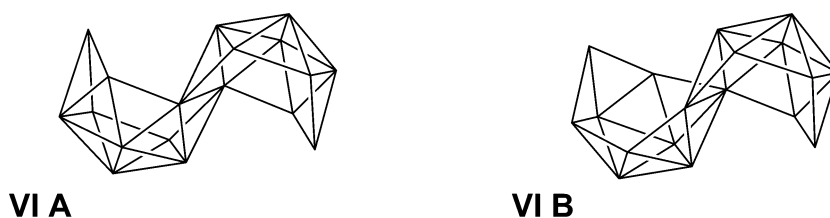
A second method of elaboration of this simple linking motif is by a multiple linking around one cluster, as in $[(SMe_2)_2B_{10}H_{10}(B_{10}H_{13})_2]$ (CCDC 162053, schematic skeleton as in **V**) [3]; see also Schematic **XX** below for further complexity based on this last theme.



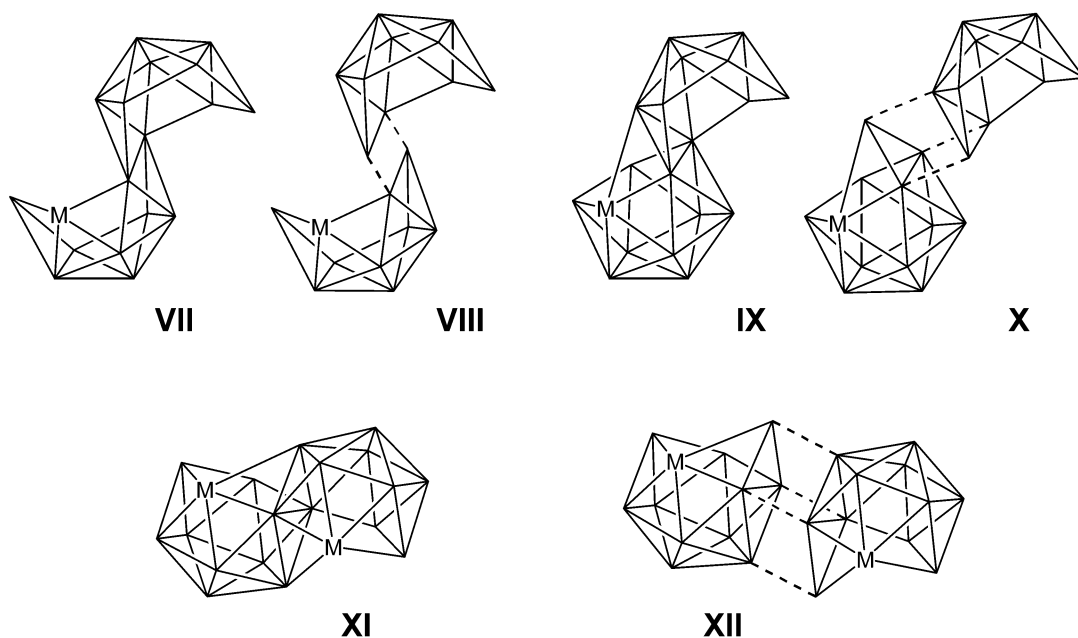
In terms of borane architectures themselves, more novelty derives from more intimate intercluster bonding involvement. Following the sigma-linked motif just mentioned, the next higher degree of intimacy is that of clusters joined together with one atom in common, for example, in $[(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2]$ (CCDC 198685, schematic cluster configuration as in **IV**) [4,5]. This is another long-recognized structural motif, particularly where the common atom is that of a metallic element. Organometallic sandwich compounds such as ferrocene—two *nido* six-vertex $\{FeC_5H_5\}$ clusters joined with a common iron atom—constitute excellent non-boron-containing examples here.



The next higher degree of intimacy is represented by structures that hold two atoms in common between two clusters. With this and higher degrees of intimacy, in which the multicenter bonding properties of boron extend through the contiguous intercluster fusion linkage, the term “macropolyhedral” is often used. Although two-atoms-in-common is another long-recognized structural motif in boron-cluster chemistry, it should be noted that rapid progress into this area is difficult: this is because there are no generally applicable generic routes to these more intimately fused multiple-cluster compounds [5,6]. In principle, a similarly difficult synthetic problem exists in carbon hydride chemistry. For example, the synthesis of, say, phenanthrene from benzene is a nontrivial task. In practice, of course, the problem is circumvented via extraction of fossil bio-deposits, etc.

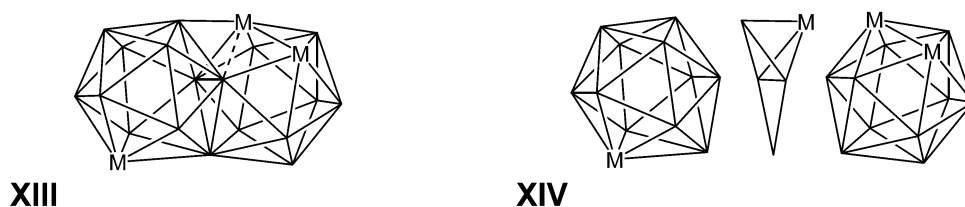


The two-atoms-in-common structural motif, together with successively more intimate intercluster fusions, is represented by products from a series of reactions of the organo-metallic halides $[(C_5Me_5)RhCl_2]_2$, $[(C_5Me_5)IrCl_2]_2$, $[(C_6Me_6)RuCl_2]_2$, and $[(^{150}PrC_6H_4Me)RuCl_2]_2$ with *syn*- $B_{18}H_{22}$ and *anti*- $B_{18}H_{22}$ [6,7]. The $B_{18}H_{22}$ isomers themselves are two-atoms-in-common macropolyhedrals (Schematics **VI A** and **VI B**). A product from one of these organometallic reactions, $[(^{150}PrC_6H_4Me)RuB_{17}H_{19}]$ (CCDC 198874, Schematic **VII**), also illustrates the same structural motif, of two *nido* ten-vertex units fused with two atoms in common (Schematic **VIII**). The next stage of intimacy, three atoms in common, is represented by $[(C_5Me_5)IrB_{18}H_{20}]$ (CCDC 101291, Schematic **IX**). The architecture is readily visualized in terms of a *nido* 12-vertex unit and a *nido* 10-vertex unit fused with 3 atoms in common (Schematic **X**).

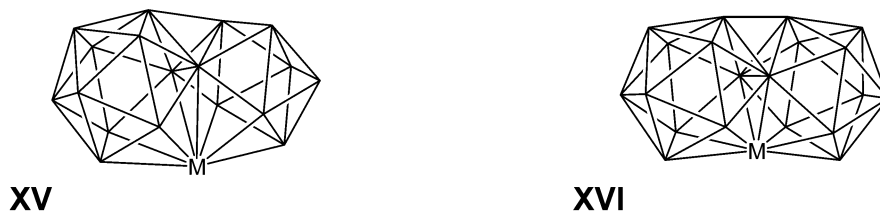


The next stage of inter-cluster condensation, four-atoms-in-common, is demonstrated by the bimetallic species $[(C_6Me_6)_2Ru_2B_{18}H_{18}]$ (CCDC 198876, Schematic **XI**). Here, the architecture can again be readily visualized in terms of 2 single-cluster subunits, now 2 *nido* 12-vertex units fused with 4 boron atoms in common (Schematic **XII**).

An even higher degree of intimacy is illustrated by $[(C_5Me_5)_3Ir_3B_{18}H_{15}(OH)]$ (CCDC 138694, Schematic **XIII**) [7]. By this stage, however, the intimacy of this very condensed intercluster fusion is such that any individual single-cluster architectures are essentially lost, and motifs of a new type of globular supermolecule architecture start to emerge. In particular, there is now the incidence of a central tetrahedrally based core structure to the cluster (Schematic **XIV**).

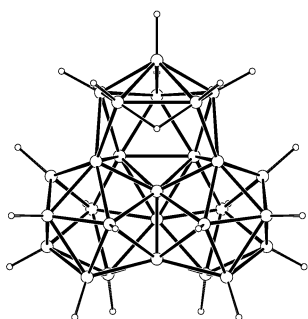
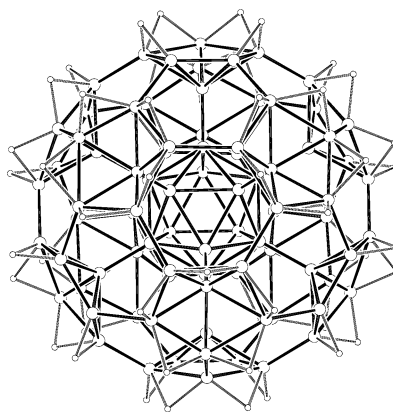
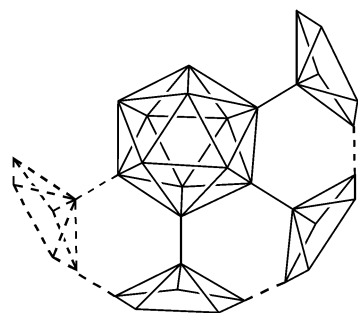
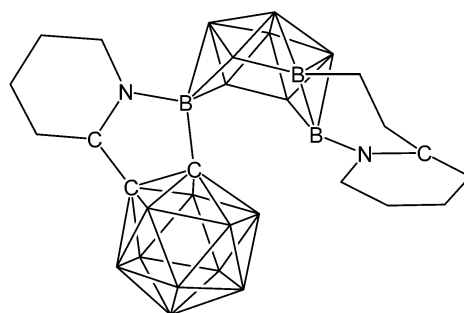


This core feature is echoed in other highly condensed macropolyhedral species, such as in the $\{IrB_{18}\}$ unit of $[(CO)(PMe_3)_4Ir_2B_{26}H_{24}]$ (CCDC 182/361) (Schematic **XV**) [8], and in the $\{PdB_{20}\}$ unit of $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$ (CCDC 111909) (Schematic **XVI**) [9].



The central borons-only cores evident in **XV** and **XVI** lead to ideas that a future large globular boron-hydride family of “megaloboranes” would be based on central borons-only cores surrounded by a boron-hydride sheet or skin [10]. These “filled-ball” species would contrast to the “hollow-ball” fullerenes, in that the centers of the molecules would need to be full of boron atoms, and not hollow. A useful premise here is that many cluster molecules can be envisaged as fragments of metallic or ceramic matrices with their peripheral valencies bound by appropriate ligands. Following this idea, calculational examination of fragments of elemental boron lattices, with the peripheries of the fragments bound by hydrogen atoms, has revealed wells of stability that could represent future synthetic targets. These include the concept molecules $B_{27}H_{21}$ and $B_{84}H_{54}$ (Schematics **XVII** and **XVIII**) [9,10].

Inspection of the structure of $B_{84}H_{54}$ (Representation **XVIII**) suggests that one synthetic approach to such species would be to assemble boron hydride units around a central boron hydride core, and then subsequently eliminate dihydrogen (Schematic **XIX**). Structures such as that of $[(SMe_2)_2B_{10}H_{10}(B_{10}H_{13})_2]$ mentioned above (Schematic **IV**) go some way in this direction, albeit not very far at present. In this vein, structures such as that of $[(CH_2CH_2C_5H_4N)B_{10}H_{10}(NC_5H_4)C_2B_{10}H_{10}]$ (CCDC 173671) (Schematic **XX**) engender the associated idea of boron hydride skins around central carbon cores [11].

**XVII****XVIII****XIX****XX**

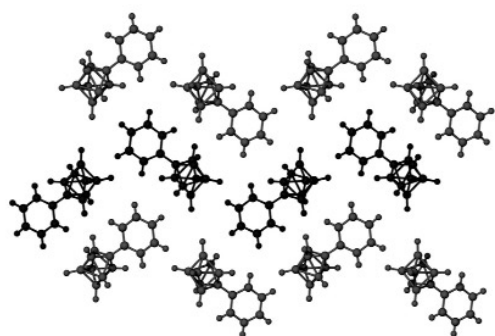
These large “megaloborane” boron-hydride species would form part of an overall fundamental boron-hydride continuum ranging from hydrogen-rich (and electron-rich) $[BH_4]^-$ through increasingly condensed and progressively hydrogen-poorer (and increasingly electron-poorer) species, $[B_3H_8]^-$,

B_5H_9 , $B_{10}H_{14}$, $[B_{12}H_{12}]^{2-}$, $B_{20}H_{16}$, etc., ultimately to hydrogen-zero elemental boron itself. This series of diminishing hydrogen content exemplifies the concept that the increasing condensation associated with increasingly intimate cluster fusion is essentially an oxidative process [10].

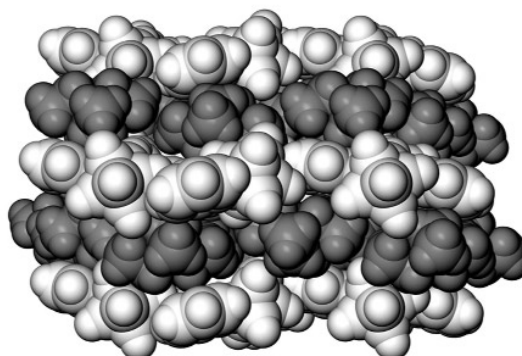
The larger globular species also exhibit interesting surface phenomena, both intramolecular and intermolecular. Examples of intramolecular surface effects include the restricted rotation of the $\{PMe_3\}$ units on the iridium atom that is held in a surface crevice of the $\{B_{18}\}$ core unit in $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ (Schematic **XV**) [8,10], and the fluxionality of the $\{(PPh_3)Pd(PPh_2)Pd(PPh_2)Pd(PPh_3)\}$ chain that snakes back and forth over the surface of the $\{PdB_{20}\}$ core (Schematic **XVI**) in $[(PPh_3)_2(PPh_2)_2Pd_3B_{20}H_{16}Pd(PPh_3)]$ [9]. The more extensive surfaces of these bigger molecules can have other surface characteristics that can engender interesting intermolecular phenomena. These include intermolecular surface-to-surface cohesion and thence directed solid-state assembly. This latter type of phenomenon initially attracted our attention in the intimate polyanionic layers in the crystals of salts of isomers of the $[Pt(B_{18}H_{20})_2]^{2-}$ anion. These last species exhibit close anion–anion sub-Van der Waals contact in the solid-state structures [12]. At about the same time, we also noted interesting intermolecular stacking in the crystal structure of the neutral species $[5-(NC_5H_5)-arachno-B_9H_{13}]$ (incidentally a previously unrecognized type in the LB_9H_{13} family) [13]. It is likely that the intermolecular associations of these and other ionic and neutral macropolyhedral species will reveal much interesting intermolecular behavior, particularly if mutually interactive cluster surfaces can be engineered by molecular design for high complementarity.

SUPRAMOLECULAR ASPECTS: NONCOVALENT INTER-CLUSTER INTERACTIONS

As a background to the last idea in the paragraph above, we have become interested in the assessment of the types of individual intermolecular interactions that could accumulate to engender big-molecule/big-molecule cohesion. There is no doubt that interesting and potentially useful intermolecular phenomena can readily arise in suitable systems. A selection of interesting possibilities can be gleaned from consideration of the four examples below. One approach here is to examine systems based on simpler molecules, in which individual atom–atom intermolecular interactions are better isolated and thence better assessed [15]. For example, an anion layering phenomenon related to that mentioned above for $[Pt(B_{18}H_{20})_2]^{2-}$ occurs in the much simpler $[NEt_4]^+$ salts of essentially all of the known seven simple monocarbaborane anions [14] of general formulation $[PhCB_nH_n]^-$. This is here exemplified by $[NEt_4][PhCB_7H_7]$ (CCDC 172016) (Schematics **XXI A** and **XXI B**). At this point, it is convenient to note that, for the assessment of this and other types of solid-state arrangement, we have found that Kitaigorodskii's Aufbau approach to the necessary crystal structure analysis is most useful [15].

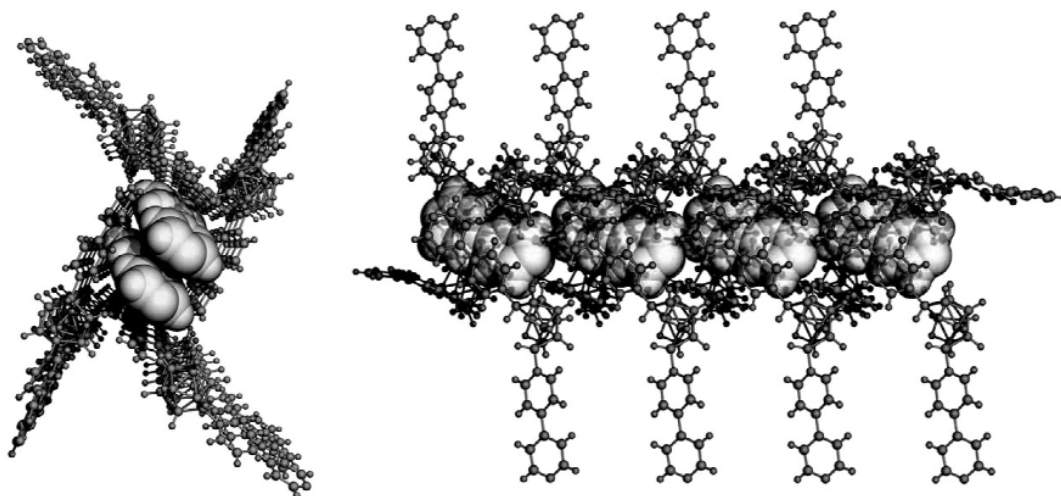


XXI A

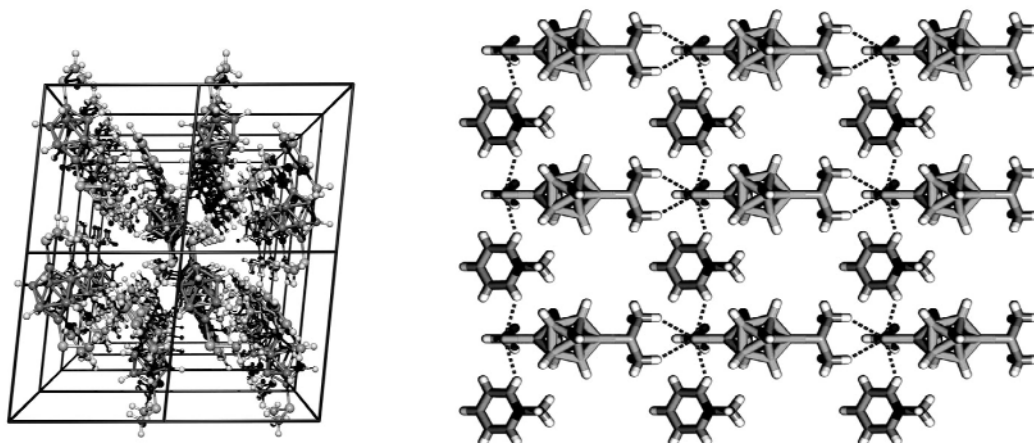


XXI B

The synthesis of $[6,9-(\text{NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_2\text{-arachno-B}_{10}\text{H}_{12}]$ (CCDC 118897) from $[(\text{Me}_2\text{S})_2\text{B}_{10}\text{H}_{12}]$ and an excess of 4,4'-bipyridyl generates the first example of more interesting supramolecular behavior [2]. From this system, it is not easy to crystallize the pure product when excess bipyridyl is present. This is because there is a preferential co-crystallization with bipyridyl. The structure of the resultant co-crystal is characterized by a double column of bipyridyl molecules that is encapsulated by a “wrap-around” progression of encapsulating $[(\text{NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N})_2\text{B}_{10}\text{H}_{12}]$ molecules (CCDC 172365, Structures **XXII A** and **XXII B** below). Clearly, if the factors behind this and the layering phenomenon of **XXI** above can be understood, and thence used for the fine-tailoring of molecular design, then further interesting and perhaps potentially useful structures may emerge, for example as precursors of specialist ceramics of specific nanomolecular character.

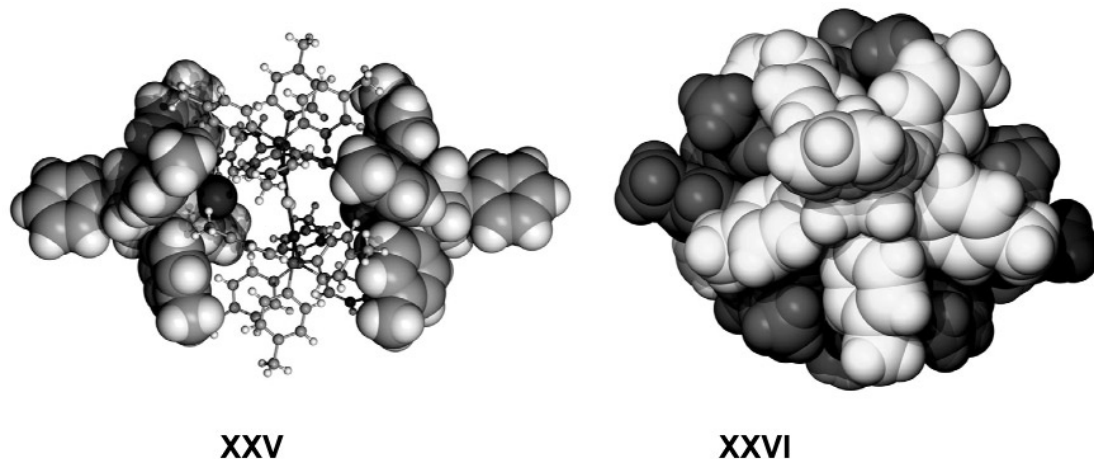
**XXII A****XXII B**

A second interesting example is afforded when the $[\text{MeNC}_5\text{H}_5]^+$ salt of the $[1-(\text{SMe})\text{-closo-B}_{10}\text{H}_8\text{-10-(SMe}_2)]^-$ anion (CCDC 172366) is crystallized with *n*-hexane present. The resultant crystal lattice is characterized by a series of parallel channels (Structure **XXIII**), bounded by a hydrogen-bonded wall of interacting cation and anion units (e.g., Structure **XXIV**), the channels being occupied by disor-

**XXIII****XXIV**

dered hexane molecules at an incidence of approximately one per unit cell [16]. If this type of phenomenon can be engineered with channel walls consisting of molecules that have functional groups with cross-linking capability, then the path may be open via thermal curing to tailored mesoporous materials.

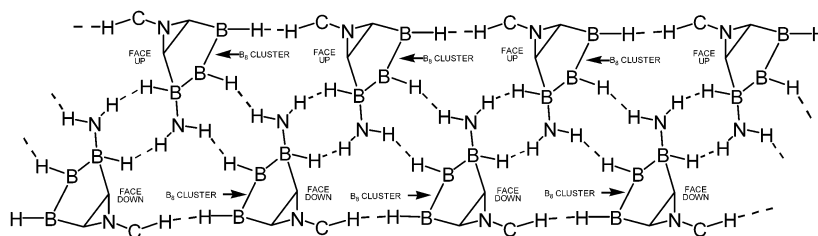
A third intermolecular phenomenon is afforded by the polyarylated monocarbaborane anions $[\text{PhCB}_9\text{H}_4\text{I}(p\text{-Tol})_4]^-$ and $[\text{PhCB}_{11}\text{H}_5\text{I}(p\text{-Tol})_5]^-$. Their method of synthesis, from the polyiodinated $[\text{PhCB}_9\text{H}_4\text{I}_5]^-$ and $[\text{PhCB}_{11}\text{H}_5\text{I}_6]^-$ anions with an excess of *para*-tolyl Grignard reagent in the presence of $[\text{PdCl}_2(\text{PPh}_3)_3]$, also engenders the formation of the $[\{\text{P}(p\text{-Tol})_3\}_4\text{Pd}_2\text{I}_2]^{2+}$ dication [14,17]. In each case, separation of this cation from the corresponding polyarylated anion has so far proved to be difficult. Elements of this difficulty may arise because there is a favored cation–anion interaction in the solid state, in which the dication is sequestered by two encapsulating anions, one on either side (CCDC 184234 and 184239). The *para*-tolyl groups generate a cavity into which the dication appears to position itself comfortably, and the *para*-tolyl groups of anion and cation then intermesh to form what appears to be a very tight assembly (e.g., Structure **XXV**). The anions have the overall appearance of a starfish or cephalopod such as an octopus entrapping its prey (e.g., Structure **XXVI**).



Here, however, $[\text{PhCB}_9\text{H}_4\text{I}(p\text{-Tol})_4]^-$ and $[\text{PhCB}_{11}\text{H}_5\text{I}(p\text{-Tol})_5]^-$ have only four and five encircling arms, respectively, and so could be visualized as “tetrapus” and “pentapus” cation predators, rather than eight-armed “octopus” species. The method of synthesis is in principle applicable to other Grignard reagents [14], permitting a fine-tuning of the encapsulating properties, with obvious implications for cation sequestration applications and other supramolecular assembly phenomena.

An important intermolecular binding phenomenon in borane chemistry that should be mentioned as part of this overview is that of dihydrogen bonding. Electronegativity considerations suggest that the hydrogen atom in a B–H unit will be relatively negatively charged, and the hydrogen atom in, for example, an N–H unit will be relatively positively charged. The resultant interhydrogen interaction—the “dihydrogen bond”—is significant, and can have a marked effect on physical properties, such as the 285° difference in melting point between H_3NBH_3 and its molecularly isoelectronic and isostructural congener H_3CCH_3 . The very dipolar isoelectronic analog H_3CF also melts at a much lower temperature than H_3NBH_3 , this difference being of comparable magnitude, at 244°. One intriguing manifestation of this phenomenon is the “inorganic nucleic acid” type of dihydrogen-bonding matrix seen within and between the chains in the so-called “chiral spiral” double helical progressions within the solid-state structures of both racemic and (+) forms of enantiomeric $[(^{150}\text{PrNH}_2)_8\text{B}_8\text{H}_{11}\text{NH}^{150}\text{Pr}]$, for which the inter-chain connectivities are schematically represented in **XXVII** [18].

XXVII



CONCLUSIONS

In summary, it is clear that the already fascinating area of single-cluster boranes, including carboranes, heteroboranes, metallaboranes, and so on, can be extended considerably in its variety of structural and chemical behavior, both realized and potential, by the ways in which individual single clusters can interact. Chemistry afforded by covalent binding can progress from molecular chains through increasingly more intimate cluster “macropolyhedral” fusions that ultimately result in very condensed globular “megaloborane” possibilities. Ostensibly weaker noncovalent intermolecular attractions, which cumulatively can engender strong intermolecular cohesion, can result in interesting and potentially exploitable layering and encapsulating phenomena and other intriguing new supramolecular effect chemistry.

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