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THE METALLIC FACE OF BORON

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I. Introduction

Textbooks of inorganic chemistry justifiably treat the element boron as a nonmetal (*1*). But from a certain point of view this is unfortunate as such a restrictive definition hides the ways in which boron mimics metallic systems. A more flexible definition of boron reveals features of its chemistry that are of significant consequence in developing an understanding of the behavior of boron-containing compounds, particularly boron–transition-metal systems. In the following, we consciously stress those aspects of boron and borane chemistry that are closely allied to transition metal chemistry. The result is interesting in a pedagogical sense and serves to draw connections between metallaborane chemistry, a developing area, and solid state metal borides, a much older area, in terms of bonding as well as practical synthetic chemistry.

Like many very general terms, the word metal is used in different ways. Elements are said to be metals when they exhibit properties (e.g., conductivity) associated with the metallic state. A more complete discussion of the definition of metallic behavior follows in Section I,A. We might say boron acts like a metal when it can be made to exhibit metallic properties. But pure element chemistry is rather limited, and chemists are interested in combinations of elements in compounds. Beyond solid state substances we might suggest metallic behavior for boron compounds when the geometric and electronic structures show similarities to those of compounds containing metals. The best comparision of this type obtains when a single compound contains metal and boron atoms that interact directly. But this point of view can be reversed. That is, when boron acts like a metal in the sense of structure and mode of bonding in a discrete molecule it may be equally valid to view the metal as acting like a nonmetal (i.e., boron). Despite such semantic difficulties, we hope to establish that the similarities of boron chemistry and metal chemistry find expression in the mixed metal–boron compounds already known. Further, these similarities suggest that considerable scope still exists for the synthesis of metal–boron compounds with unusual properties ranging from metallic to nonmetallic. It is noteworthy that early studies of the electronic structure of boranes placed them in a class between ordinary covalent compounds and the metals (*2*) and that the *Journal of Less Common Metals* regularly includes papers on boron.

This chapter has a number of interpenetrating themes. First the properties of the element are reviewed and an idea of the relationship of boron to the other elements in terms of metallic character is developed. Next we present structural evidence delineating the similarities and differences of borane and transition metal species. Pertinent examples from metallaborane chemistry demonstrate real bridges between the two distinct areas. Both discrete and solid state systems are discussed and the transition metal borides constitute bridges in the latter case. As will be seen, despite real differences due to the differing electronic structures of the atoms, there are a considerable number of similarities between the structural elements of the discrete complexes and the repeating units in the solid state. This theme receives further emphasis in a discussion of discrete transition metal borides that constitute links between molecular species and solid state structures with extended bonding networks. Finally, we briefly discuss how such discrete metallaboranes provide a logical preparative approach to solid state materials containing transition metals and boron.

A. DEFINITION OF A METAL

Although the element boron is properly labeled as a nonmetal, its designation as such needs qualification even for the element itself. In a general sense this point was emphasized by Edwards and Sienko some time ago, and they have adopted a straightforward criterion based on atomic properties to distinguish metals from nonmetals (*3*). The simple Edwards–Sienko definition is "If the mutual polarization of an atom by the remaining atoms in the condensed phase is sufficiently strong, that is, when the individual atoms are sufficiently large or their density sufficiently high, the valence electrons are set free and the system acquires metallic status." (*4*). This view of metals is one in which atomic size is a crucial property and, hence, is a very appealing one to chemists. In contrast to criteria based strictly on the collective physical properties of substances under ordinary conditions, it also provides insight on the relative ease of transforming a nonmetallic substance into a metallic one.

To sketch out the Edwards–Sienko approach, let us begin with Mott's original picture of the transformation of a nonmetal into a metal and the reverse (*5*). Consider a system consisting of a simple array of hydrogen-like cations (M^+) plus an equal number of electrons (e^-). Coulomb's law requires the existence of a tendency for the formation of cation-electron pairs (M^+,e^-). If the binding energy of the (M^+,e^-) pairs is large, the material is nonconducting; whereas if the binding energy is zero, the electrons constitute an itinerant electron gas in which the cation lattice is immersed. The binding energy of the (M^+,e^-) pairs will depend on the effectiveness of the screening of the interaction of a $M+$ cation with an e^- by all the other electrons. That is, the electron gas acts like a dielectric, and for the metallic state the dielectric constant approaches infinity. The effectiveness of this screening will increase as the individual atoms become larger or as the density increases.

In representing the strength of the (M^+,e^-) interaction, Edwards and Sienko, using an approach due to Herzfeld (*6*), derive Eq. (1) as an expression for the frequency of the bound electrons;

$$\nu = \nu_0[1 - (R/V)]^{1/2} \qquad (1)$$

where V is the molar volume in the condensed state (1 atm pressure and room temperature, or the melting point of the substance if lower than room temperature) and R is the molar refractivity of the gaseous state. As R/V approaches one the strength of the (M^+,e^-) interaction approaches zero; that is, the system becomes metallic. Now $R = (4/3)L\pi\alpha$, where L = Avogadro's number and α is the polarizability which was taken to be constant by Herzfeld for all densities up to the onset of metallic behavior. The dependence of metallic behavior on molar volume thus becomes clear. Metals will have $R/V < 1$ and nonmetals will have $R/V < 1$. In Fig. 1 R/V values for the elements under normal

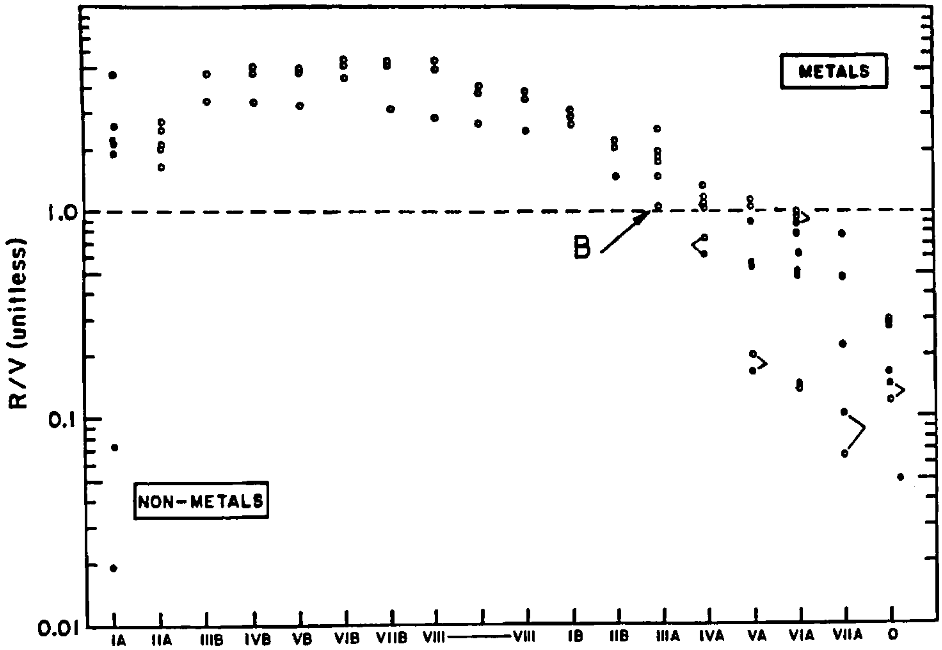

FIG. 1. Plot of (R/V) for elements where R is the molar refractivity and V is the molar volume. The filled points represent elements for which both R and V are known experimentally; the open circles are for elements for which V is known experimentally and R is calculated. (Reprinted with permission from Edwards, P. P., and Sienko, M. J., *J. Chem. Ed.* **69**, 691 (1983). Copyright 1983 American Chemical Society.)

(planet earth) conditions are displayed, and one notes a range of values with a considerable number of elements at the borderline of $R/V = 1$. Among these borderline elements is boron. In fact the stated R/V is slightly greater than one but, unfortunately, the R value used was a calculated rather than experimental one.

The energy necessary to transform boron from the nonmetallic to metallic state has been estimated (*7*). In a study of the enthalpy of formation of borides and related compounds the transformation energy has been estimated as 30, 100, 240, 33, and 50 kJ/Mol for B, C, N, Si, and P, respectively (*8*). This provides another measure of how close the element boron is to the metal and nonmetal borderline.

Eq. (1) also suggests that a nonmetal-to-metal transition can be effected by increasing the normal density of the system. Indeed the metallization of molecular H_2 is cited as a spectacular example of such a transformation (*9*). But the R/V of H_2 is an order of magnitude lower than that for boron. Hence, much smaller density changes should be effective in converting elemental boron to metallic behavior. Moving a step away from the pure element, some two component systems transform from nonmetallic to metallic behavior at a critical concentration. The classical example is the Na–NH_3 system. At 298 K the critical concentration for the transition is at about 1 mole percent sodium, with solutions of lower concentration being nonmetallic (*10*). Clearly, as the chemical complexity of a system increases the strictly elemental properties become only a partial determinant of overall system behavior. This point is underlined by the fact that, although a number of elements are superconducting at low temperatures, the high-temperature superconductors, which are the subject of intense technical and popular scrutiny these days, possess a complex chemical architecture. Hence, the search for useful organic metals constitutes a reasonable research objective, and there should be equal or even more scope for metallic substances based on boron.

B. SOURCES OF COMPARISON

First consider elemental properties. In the periodic table boron is placed on the nonmetal side of the diagonal borderline formally separating metals from nonmetals. The properties of boron that justify its position may be found in any textbook of inorganic chemistry. Though black with a metallic luster, it is a semiconductor, possesses a very large entropy of melting (*11*), and is very hard. In terms of its chemistry, boron must also be classified as nonmetallic. With HCl there is no reaction, whereas other group 13 elements lying across the metal/nonmetal divide (i.e., aluminum, galium, etc.) react to yield H_2. Further the hydrides of boron and other main group nonmetals (e.g., silicon) are volatile, flammable gases, whereas that of aluminum, for example, is polymeric.

On the other hand, in Hume-Rothery's classification of the elements boron is one of two placed in its own box as neither metal, intermediate element, or nonmetal (*12*). Indeed, there are properties of boron and features of boron chemistry that are similar to those of transition metals. The electronegativity of boron is less than that of hydrogen as is the electronegativity of most transition metals. This property is also common to other nonmetals past the first row (e.g., silicon). There is, however, one crucial difference between boron and other elements such as silicon. Because it lies to the left of carbon, boron has fewer valence electrons than valence orbitals. Elements with this electronic feature are usually found to exhibit metallic bonding in the elemental state but the small size of boron precludes this. However, like a transition metal, it exhibits a pronounced tendency to form Lewis base adducts. The number of base moieties added is usually one, in constrast to a transition metal where six is a common ligand capacity. This coordination chemistry is outlined more fully in Section II,A. Of course, elements such as silicon can also exhibit unsaturated behavior in that the empty *d* shell is sufficiently low-lying to affect, for example, reactivity. Still, for boron, unsaturation results from an empty valence orbital that is of sufficiently low energy that BH_3 spontaneously dimerizes to B_2H_6; that is, even a B–H bond is a good electron pair donor to an empty B_{2p} atomic orbital. This is not the case for SiH_4, which exists as a monomer.

Boron, with a partially filled $n = 2$ shell, exhibits a pronounced tendency for covalent bonding even though the valence orbitals are more diffuse than those of carbon. Transition metals with very diffuse $(n - 1)d$, *ns*, and *np* orbitals have a greater tendency than boron toward ionic bonding and the formation of high-oxidation-state coordination complexes. It is not that long ago that discrete compounds containing bonds between metal atoms were referred to as "a new mode of transition metal chemistry" (*13*). However, both boron and metals exhibit homonuclear bonding, albeit multicentered, in catenated structures. That is, the homonuclear compounds of boron and transition metals tend to possess three-dimensional cluster structures rather than the rings and chains of electron precise or electron rich elements. As this is clearly one area of distinct similarity, the comparisons between metals and boron are developed more fully in Section II,B.

Finally, the structural modifications of elemental boron exhibit complex extended lattices of cages in the solid state, whereas those of metals possess much simpler close-packed atomic lattices. These differences are a direct reflection of atomic properties and result in the respective nonmetallic and metallic behavior. However, boron combines with most other elements including metals. There are a wide range of metal borides known with stoichiometric as well as nonstoichiometric atomic ratios. The amazingly varied interpenetration of the two characteristic structural motifs and the subtly balanced competition between the two modes of solid state bonding found in the metal borides constitutes further justification of our theme. This is discussed in some detail in Section II,C.

II. Comparison of Geometric and Electronic Structures

Historically, the spatial arrangement of nuclei in compounds has constituted the primary source of information on chemical bonding between nuclei. To a large extent this is still true today, although experiments such as those giving differential electron densities yield more detailed and direct information on the forces holding molecules and other chemical entities together. In addition photoelectron spectroscopic and theoretical studies are being successfully applied to complex systems with considerable success (*14*). Hence, to seek similarity in bonding between metal and boron compounds we first examine the evidence from structural studies, with information from other studies being included where relevant.

A. MONONUCLEAR COMPOUNDS

The discrete compounds containing single boron atoms or single metal atoms are about as far from systems having metallic character as it is possible to get. Hence, the purpose of this section is to simply draw the readers' attention to some interesting similarities between the chemistry of boron and a transition metal. One of the characteristic chemistries associated with transition metals is that of ligand coordination, and we present comparisons between a few boron and metal coordination compounds below. Even for these covalent species, the selected compounds illustrate and support the theme of this chapter.

The coordination chemistry of boron was reviewed some time ago and the structure and properties of compounds of the general formula $BX_3 \cdot L$, where X and L can be one of a wide variety of substituents and electron pair donors, respectively (*15*). Indeed, the reactions of tricoordinate boron compounds in general are thought to proceed via addition of the reaction partner in a Lewis acid–base reaction to yield a tetracoordinate intermediate that then undergoes further reaction. Stable tetracoordinate boron compounds are subject to ligand displacement reactions for which a variety of mechanisms obtain (*16*). The coordination chemistry of transition metals is vast and includes not only structural facts (*17*) but considerable information on the mechanistic behavior of these species as well (*18*). In our brief comparison we will restrict ourselves to low oxidation state chemistry and group 16 metals (*19*).

The two reactions that will serve as the basis of the following discussion are given in Eq. (2) and (3).

$$BH_3 + CO \rightarrow BH_3CO \qquad (2)$$

$$Fe(CO)_4 + CO \rightarrow Fe(CO)_5 \qquad (3)$$

Both are acid–base reactions involving in the case of boron the transcient BH_3 molecule (*16*) and in the case of iron the unsaturated transient $Fe(CO)_4$ (*20*). These two species are isolobal (*21*) in that they both have an empty, low-lying valence orbital. In both cases the forward reaction is very rapid and exothermic. In fact the Fe–CO and B–CO bond energies are also reasonably similar (125 (*22*) and 100 kJ/mol (*23, 24*), respectively). Structural changes associated with an acid–base reaction reveal the nature of the interaction (*25*). Borane is a planar species, whereas $Fe(CO)_4$ has C_{2v} symmetry and C–Fe–C angles of ~120° and 145° (*26*). In reacting with the common ligand CO the most dramatic structural change is that taking place in the Lewis acids. BH_3 and $Fe(CO)_4$ undergo ligand rearrangement toward tetrahedral boron (H–B–H angle = 113°52′) (*27*) and pentagonal bipyramidal iron atoms, respectively. Consistent with a simple acid–base reaction is a decrease in the B–H stretching frequency (*28, 29, 30*). Different behavior is observed for the metal carbonyl. The force constants calculated for $Fe(CO)_4$ increase in going to $Fe(CO)_5$ (16.55, 16.21 to 16.95, 16.57 mdyne $Å^{-1}$) (*31, 32*). There is also a difference when one considers changes in the base. For BH_3CO the C–O distance and CO stretching frequency are close to the values observed for the free ligand, whereas for $Fe(CO)_5$ and metal carbonyls in general there is an increase in C–O distance and decrease in CO stretching frequency. The electronic changes taking place in reaction (2) are not simple (*33*), and BH_3 has been discussed as a π acid (*34*). However, in terms of the magnitude of the changes observed in reaction (2), there is no equivalent to the metal-to-ligand π backbonding that is so important for the metal carbonyls. Thus, although the acid–base reactions are very similar, the presence of the "nonbonding" 3*d* electrons in the metal carbonyl results in distinctive differences in detail. Further, the photoelectron spectra for BH_3L and $(CO)_4FeL$ also demonstrate similarities in ionization potential trends with L = CO, NMe_3, and PMe_3. It is only in the case of the metal that the effects of π backbonding of the CO ligand are clearly evident in the ionizations associated with the Fe 3*d* metal MOs (*35*).

Reactions (4) and (5) constitute another pair for comparison.

$$BH_3 + H_2 \rightarrow BH_5 \tag{4}$$

$$Fe(CO)_4 + H_2 \rightarrow (CO)_4FeH_2 \tag{5}$$

Here, although $(CO)_4FeH_2$ is a well known molecule, evidence for the existence of BH_5 comes from mechanistic studies on the reaction of BH_4^- with H^+ and quantum chemical calculation (*36, 37, 38*). There are now significant differences in the structures of the products. BH_5 is described as a weakly bound adduct of H_2 whereas $(CO)_4FeH_2$ is a dihydride. Although transition metal compounds with dihydrogen ligands are now well known (*39*), there clearly is a greater tendency for "oxidative-addition" for a metal than for boron. For the H_2 bond to be broken either the σ MO must be depleted or the σ^* MO filled. The former is possible with both BH_3 and $Fe(CO)_4$, but the latter is only possible with $Fe(CO)_4$. Again the effect of the "nonbonding" *3d* electrons on the metal is important.

B. CLUSTER COMPOUNDS

Discrete metal clusters exhibit cores with structures that range from deltahedral arrangements (small clusters) to close-packed arrays (large cluster cores) (*40, 41*). On the other hand, known borane structures are all deltahedral and non-close-packed (*42*). Larger boranes are observed as terminal, edge, or face fused deltahedra. Single boron cages containing more than 12 cluster atoms have not been characterized, although they have been predicted to be stable (*43*). The relationship between the structures of the deltahedral main group and metal clusters and the number of electrons associated with cluster bonding is expressed by the electron counting rules (*44, 45, 46*). By dividing the total number of valence electrons into those associated with cluster skeletal bonding and all others (exo-cluster ligand bonding, exo-lone pairs or nonbonding electrons) connections between apparently dissimilar species become evident, for example, $[B_6H_6]^{2-}$ and $[Fe_6(CO)_{18}]^{2-}$. (The latter is presently unknown although $H_2Ru_6(CO)_{18}$ is known (*47*). Both species have octahedral cluster cores (Fig. 2) and seven skeletal electron pairs, because BH and $Fe(CO)_3$ fragments each contribute two electrons and three orbitals to cluster bonding. The cluster bonding MOs of both boron and metal clusters are intrinsically delocalized; that is, the lines delineating the cluster core do not correspond to covalent bonds. An excellent review of cluster theories in general has been presented by Mingos and Johnson (*48*).

The homonuclear cluster $[B_6H_6]^{2-}$ constitutes the exemplar of a main group cluster; the electronic structure of this dianion has been discussed in relationship to those of other cages. (*49*). As illustrated in Fig. 3, this species has 13 filled MOs of which six are associated with exo-ligand bonding and seven with cluster bonding. However, as is clear from the diagram, few of the filled MOs are purely cluster bonding (t_{2g}) or purely exo-ligand binding (e_g). Hence, for exo-ligands more complex than hydrogen atoms or for cluster fragments more complex than BH (e.g., $Fe(CO)_3$), one must be prepared for non-Wadean behavior. This is amply illustrated by the B_nCl_n clusters (*50*) and transition metal clusters in general (*51*). The poor separation of exo- and endo-cluster MOs

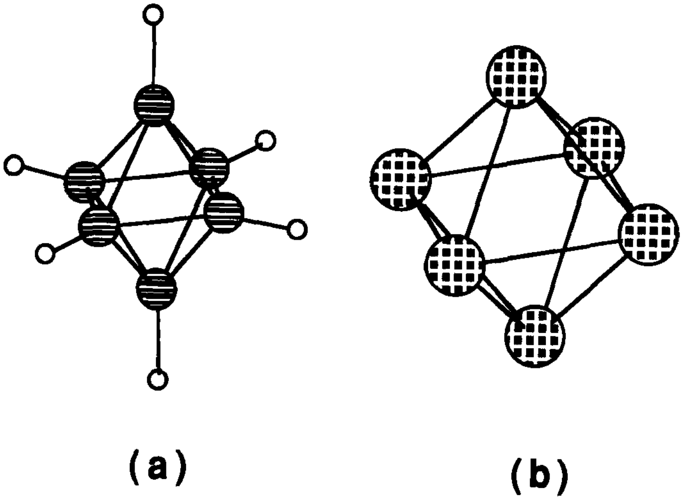

FIG. 2. Representation of the cluster structures of (a) $[B_6H_6]^{2-}$ and (b) $[Fe_6(CO)_{18}]^{2-}$, where in the latter the large spheres represent $Fe(CO)_3$ fragments.

also results in the ready transmission of substituent effects through the cage (*52*).

One can now ask the question whether the boron in $[B_6H_6]^{2-}$ is behaving like a metal or whether the metal in $[Fe_6(CO)_{18}]^{2-}$ is behaving more like boron. One way of testing is to construct the cluster bonding MOs, beginning with BH or $Fe(CO)_3$ fragments and, separately, with the bare B_6 or Ru_6 cores and the H or CO exo-ligands. The relative complexity of the two correlation diagrams for each is a measure of the relative importance of cluster bonding to exo-ligand bonding. This approach has been used for the $(CO)_9Co_3CCl$ cluster and it was shown that the fragment analysis [CCl and $Co(CO)_3$] is conceptually simpler than the other [CCo_3 and Cl + 9 CO] in this system because the formation of the Co–CO bonds is a larger perturbation than the formation of the Co–Co bonds (*53*). Thus, as the B–H and B–B interactions are of comparable strength, one expects correlation diagrams of similar complexity for the two approaches to $[B_6H_6]^{2-}$.

A second way to answer the question is to explicitly model the geometric behavior of transition metal clusters with suitably chosen boron cages and the geometry-optimization techniques of quantum chemistry. For example, the geometries of the main group model compounds $MeCC_3H_3$ and $MeCB_3H_6$ with structures generated by ab initio calculations reproduce the cluster structural differences of $Co_3(CO)_9CMe$ and

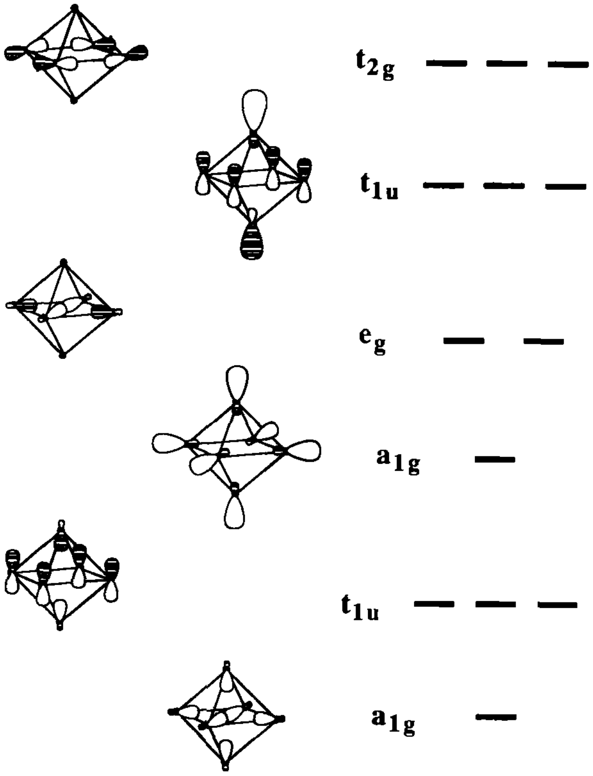

FIG. 3. The occupied molecular orbitals of $[B_6H_6]^{2-}$. For the degenerate sets only a single component is sketched.

$H_3Fe_3(CO)_9CMe$ (*54*). Likewise, examination of the series $[B_6H_6]^{2-}$, $[B_6H_7]^-$, and B_6H_8 provides an explanation for the structural changes observed in the analogous osmium carbonyl clusters (*55*). This approach has been extended to the deprotonation of HCB_3H_6, providing further insight into the formation of $[HFe_3(CO)_9(HCH]^-$ from $H_3Fe_3(CO)_9CH$ (*56, 57*). From both approaches one concludes in the case of these small cluster compounds that it is more appropriate to think of the similarity between boron and metal clusters as evidence of the nonmetallic behavior of iron rather than the metallic behavior of boron.

On the other hand as one goes from small metal clusters to large metal clusters there is an evolution of properties associated with the core from the molecular to the bulk metallic state. This relationship has been effectively summarized by Mingos (*58*). How great then is the difference between the larger borane cages and similar sized metal clusters? Consider the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ cages with bicapped square antiprismatic and icosahedral geometries, respectively. Electronically equivalent metal cluster analogues of the latter have been characterized by Dahl and co-workers; that is, $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ has a deltahedral structure with 10 Ni and 2 As forming a noncentered icosahedral cluster core (*59*). Further substitution of the two arsenic fragments with isolobal $Ni(CO)_3$ fragments generates the unknown $[Ni_{12}(CO)_{24}]^{2-}$ cluster. The known $[Pt_{12}(CO)_{24}]^{2-}$ cluster has the same electron count but has a structure consisting of the stacking of four $Pt_3(CO)_3(\mu\text{-}CO)_3$ layers (*41*), presumably because the steric requirements of the 24 carbonyl ligands are better satisfied by the observed structure.

Alternatively, one might explore close-packed structures of boranes. Consider, for example, the difference between deltahedral and tetracapped octahedral $B_{10}H_{10}$ structures (Fig. 4). The former is stable as the dianion (11 cluster pairs) while, based on Extended Hückel calculations (*60*), the latter is slightly more stable for the +6 cation (7 cluster pairs). The capping principle predicts 7 cluster pairs for capped octahedra (*61*). A structurally characterized transition metal analogue of the tetra-

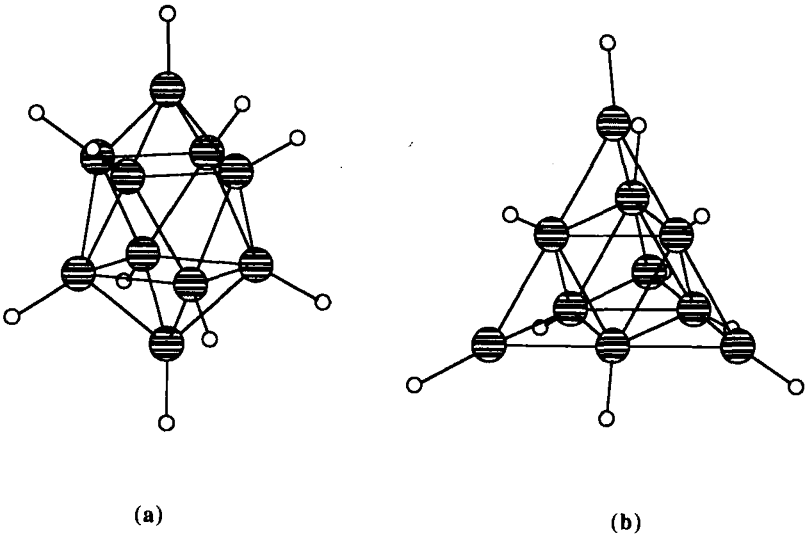

FIG. 4. Isomeric structures of $[B_{10}H_{10}]^{2-}$: (a) bicapped square antiprism and (b) tricapped octahedron.

capped octahedral boron cage with 7 cluster pairs is $[Os_{10}C(CO)_{24}]^{2-}$ (*62*). Thus, although the spatial requirements of the ligands favor close-packed structures for the larger metal clusters, there is an electronic factor that disfavors close-packed structures for boron; that is, one can vary metal fragment count by varying metal and number and type of exo-ligands but boron is stuck with 3 valence electrons and, usually, a one electron exo-ligand like hydrogen. One wonders, however, what structure $[Be_4B_6H_{10}]^{2+}$ would favor.

Finally, just as BH_3 coordinates to CO, so do a number of the higher borane cages. For example, $B_2H_4(CO)_2$ (*63*), B_3H_7CO (*64*), B_4H_8CO (*65*), and $B_{10}H_{10}(CO)_2$ (*66*) are all well characterized compounds. Because each boron atom with a coordinated CO contributes 3 electrons to the cluster count, only a few such exo-ligands can be accommodated. Dispite this, these clusters also express the close relationship between boron and transition metal clusters.

C. HYBRID SYSTEMS

1. *Discrete Metallaboranes*

We have already mentioned that because of the excess valence orbitals over valence electrons, homonuclear cluster formation readily occurs for both boron and metals and that endo-cluster bonding is intrinsically delocalized (Section II,B). However, when some of the acceptor orbitals of a metal are "tied off" with Lewis bases, the resulting metal—ligand fragments behave much like borane and other main group fragments in the manner in which they form clusters. A good test of the metallic behavior of boron, then, would be a comparison of the extent of delocalization of the endo-cluster MOs in clusters containing both metal and boron atoms; that is, how "misible" are the metal and boron AOs in forming the cluster bonding MOs? Alternatively, the extent that the endo-cluster MOs can be localized into boron, metal, and boron—metal orbitals expresses the dissimilarity of boron and metals.

The existence of mixed metal–boron clusters constitutes one example of the validity of the isolobal principles when applied to a class of compounds. The stoichiometric and structural diversity of metallaboranes is truly striking, and the idea of isolobal fragments combined with the electron counting rules is sufficient to rationalize this diversity—this fact is impressive (*67, 68, 69, 70, 71, 72, 73, 74*). We have explored the mixing of boron and metal characters in cluster MOs in the $B_5{}^{-}{}_{n}H_{9-n}[Fe(CO)_3)]_n$ nido cluster series (Fig. 5). Examples of the first four members of this series (a, b, c, and d) have been well characterized (*75, 76, 77*), and suggestive evidence has been published for a $B_2H_6Ru_3$-

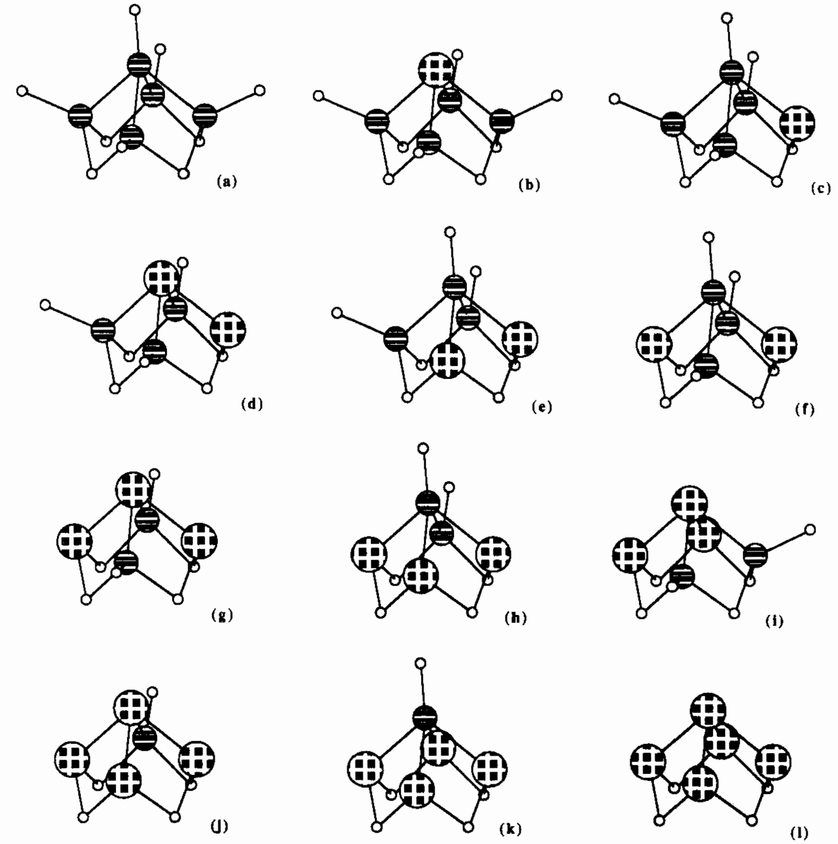

FIG. 5. The possible geometric isomers of $B_{5-n}H_{9-n}[Fe(CO)_3]_n$ assuming a square pyramidal cluster core.

$(CO)_9$ (*78*). The dehydrogenated analogue of $BH_5Fe_4(CO)_{12}$, $HFe_4(CO)_{12}BH_2$ (*79*) has been characterized and a carbon analogue of $H_4Fe_5(CO)_{15}$, $Fe_5C(CO)_{15}$ (*80*) exists. In some earlier work we addressed this question by focusing on the B_3 fragment in $B_3H_7Fe_2(CO)_6$ compared with B_3 fragments behaving in a distinctively ligand-like manner (*81*). We found that in a relative sense the scrambling of metal and boron fragment orbitals increased in the order $(CO)_2NiB_3H_7 < (CO)_4MnB_3H_8 < (CO)_6Fe_2B_3H_7$. The polarization of electronic charge between the metal and borane fragments also measures relative mixing of boron and metal fragment orbitals. Here the order found was $(CO)_4MnB_3H_8 < (CO)_2NiB_3H_7 < (CO)_6Fe_2B_3H_7$. In related work we showed that in the comparison of the photoelectron spectra of three members of the series in Fig. 5 (a, b, d) there is a smooth correlation between the bands associated with cluster bonding and a decrease in ionization potential as metal content increases (*82*). Thus, there is a suggestion that metal and boron fragments are very compatible cluster fragments; this may account for the substantial, growing number of metallaboranes characterized.

Finally, for completeness, note that in metallaboranes containing metal carbonyl fragments one also finds CO bound to boron. The spectroscopically characterized cluster, $B_5H_3(CO)_2Fe(CO)_3$ (*83*) exhibits two boron bound CO ligands, whereas the crystallographically characterized $H_3Os_3(CO)_9BCO$ cluster exhibits one CO bound to the apical boron atom (*84*). The boron-bound CO on the latter cluster undergoes displacement by PMe_3 and reduction to a "borylidene" fragment by reaction with $BH_3 \cdot THF$ (*85*) Quantum chemical and photoelectron spectroscopic studies provide further evidence that the capping boron atom behaves as a pseudo-metal atom (*86*).

2. *Metals, Boron, and Metal Borides in the Solid State*

The metal borides are one of the five major classes of boron compounds (*1*). In the following we review the geometric and electronic structural data with an emphasis on the transition metal borides. Because the structures of transition metals and elemental boron provide end points, we begin by reviewing the solid state structures of these elements. A brief survey of the range of metal boride structures in general is followed by some more detailed consideration of the problems of electronic structure raised by the geometries of the transition metal borides.

a. Structures—Metals vs. Boron. Metals constitute about two-thirds of the known elements and, with only a couple of exceptions, crystallize in face-centered cubic, hexagonal close-packed and/or body-centered cubic lattices. The single element boron, on the other hand, is found in a number of allotropic forms with rather complex structures (*87*). A simplfying feature of the known crystalline structures is the nearly ubiquitous presence of the B_{12} icosahedron (Fig. 6). For example, the solid state structure of α-rhombohedral boron may be described as a nearly cubic close-packed array of approximately regular B_{12} icoahedral cages. An idealized drawing of the spatial arrangement is shown in Fig. 7. Because the "bonds" between the icosahedra are weaker than those within the icosahedra, the B_{12} cages might be viewed as ~6 Å diameter covalently bound spheres in a close-packed metallic-like lat-

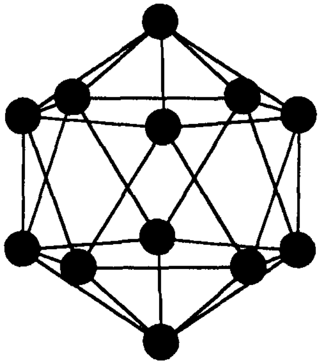

FIG. 6. The icosahedral geometry of $[B_{12}H_{12}]^{2-}$ where the solid spheres represent BH fragments.

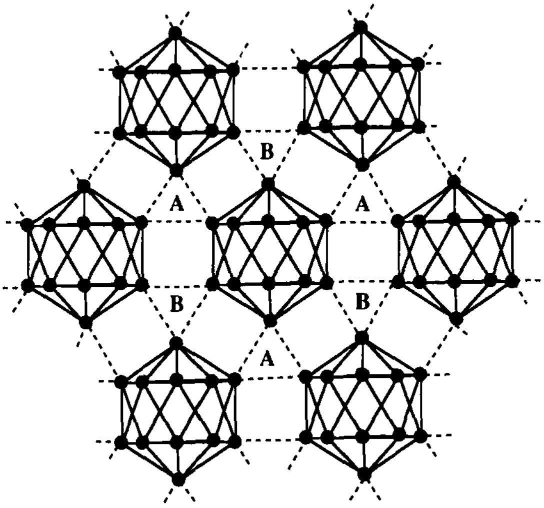

FIG. 7. A representation of the basal plane of α-rhombohedral boron consisting of close-packed icosahedral of boron atoms. The triangles defined by dotted lines represent three-center bonds between the icosahedra in the plane involving six of the twelve boron atoms. The remaining boron atoms (three above and three below the plane) are bonded by two-center bonds to sheets of icosahedra centered above the point marked A or below point B.

tice. However, it appears that the structure of the β-rhombohedral crystalline form of boron is the thermodynamically most stable atomic arrangement. The crystal structure exhibits much more complexity but the icosahedral theme is still very much present. One can see in a model of the structure an icosahedron that is in turn surrounded by an icosahedron of icosahedra. In the partial representation shown in Fig. 8 the basic unit consists of a central icosahedron, each boron of which has an exo-bound icosahedron of boron atoms attached to it. These clusters of clusters are connected by fusing exo-icosahedra to the exo-icosahedra of the nearest neighbor cluster of clusters. The 10-atom fragment in Fig. 8 shows the geometry at the intersection of these exo-icosahedra. Nine of the boron atoms in the form of four fused pentagonal rings surround a central nine-coordinate boron atom. Finally there is one additional type of boron atom located at a center of symmetry between two adjacent 10-atom fragments. Each unit cell contains the central icosahdron (12 B), 12 exo-icosahedra with the outer six atoms lopped off (72 B), two of the 10-atom fragments (20 B) and one of the special borons giving a total of 105 atoms. The fused cages lead to a strongly bound covalent network and accounts for the refractory nature of the elemental material.

One can imagine an unstable form of boron with atoms arranged in a close-packed metallic lattice. Although this form is unknown, it would

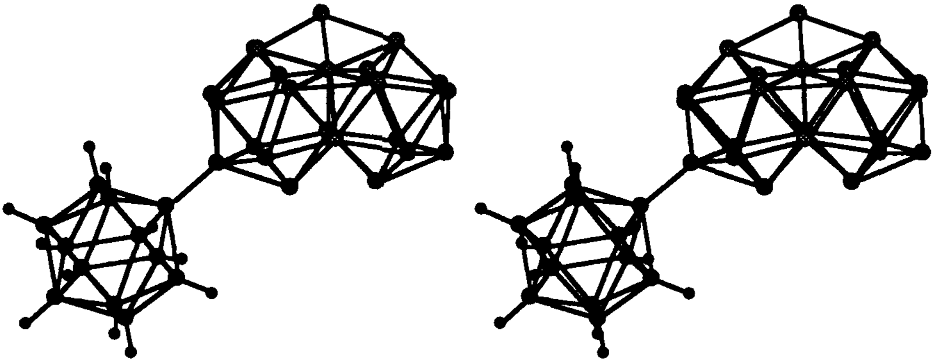

FIG. 8. A stereoscopic sketch of important elements of the structure of β-rhombohedral boron. The dots on lines extending in radial directions from the icosahedron at the left represent connections to exo-icosahedra, only one of which is shown. The 10-atom fragment mentioned in the text is shown by the lightly shaded spheres in the structure to the right consisting of fused icosahedra.

be unstable with respect to a close-packed lattice of covalently bound icosahedra of boron atoms (α-rhombohedral boron), which in turn is unstable with respect to a completely covalently bound lattice of icosahedra of fused icosahedra (β-rhombohedral boron). The tendency for boron towards covalent bonding vs. metallic bonding in the solid state (small size and high ionization potential) clearly wins out for the element, but the competition takes some interesting turns when boron is combined with true metals to form the metal borides.

b. Structures—Metal Borides. Because of their technological value as well as promise the metal borides have received considerable attention (*88, 89, 90, 91*). Several hundred binary borides are known; they range in stoichiometry from M_5B to MB_{12} and higher. Nonstoichiometric phases of variable composition and ternary compounds add to the list of interesting systems. In addition, as corrections to previously published results continue to appear (*92*), some uncertainty is added to an already complex situation (*93*). As is often the case in solid state systems stoichiometry is less informative than structure simply because there is no immediately evident relationship between the two. In fact, because the boron network takes up characteristic forms, it has often been found more useful to classify the borides according to the type of boron network rather than according to stoichiometry per se (*94*). In what follows our intention is to illustrate some of the ways metals and boron "mix" structures rather than to comprehensively enumerate all reported compounds.

We have already pointed out that the most stable forms of the solid state bonding of elemental boron and metals differ in an essential aspect. Hence, in the solidification of a melt containing a random mixture of metal and boron atoms the observed structure will be determined by a balance between the tendencies for boron to form a covalently bound network and the metal to form a close-packed lattice. Among other things, this competition will depend on relative metal and boron concentrations and one expects in proceeding from the metal-rich to the boron-rich borides that the B–B bonded network will become more extensive and dominant.

With the exception of some special cases, two major classes of structure can be distinguished. In the first, the metal-rich borides possess boron atoms at the centers of trigonal prisms of metal atoms, and the boron atoms interact in one- or two-dimensional homonuclear networks. This class covers the range of stoichiometries from M_3B to MB_2. Presumably these structures, particularly those containing the highest metal-to-boron ratio, are controlled by the requirements of the metal lattice. Indeed the metal atoms are found in an approximately hexagonal arrangement. Such a lattice is approximated, as shown schematically in Fig. 9a, as fused trigonal prisms containing centered atoms. As shown in Fig. 9b, each centered atom has six nearest neighbors in a trigonal prismatic arrangement and three next nearest neighbors (*p*, *q*, and *r*) in a trigonal arrangement. As indicated in Table I, depending on the identity of *p*, *q*, and *r* (boron or metal atom), representations of structures containing isolated boron atoms to planar nets and stoi-

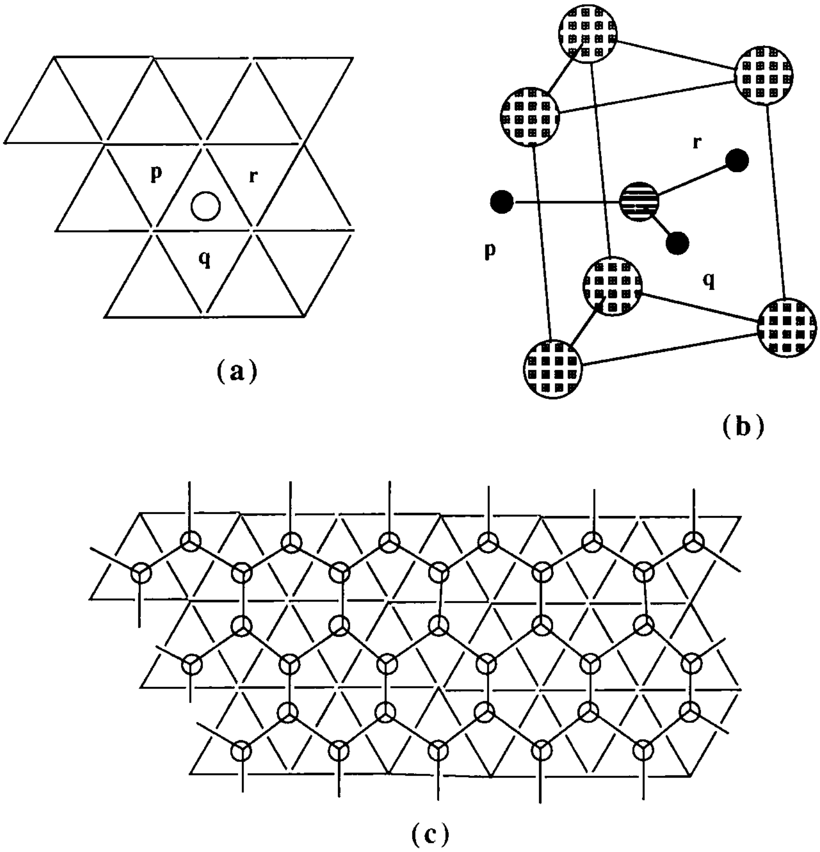

FIG. 9. (a) Arrangement of trigonal prisms in a close-packed structure showing a boron atom in one trigonal prismatic hole and the locations of the next nearest neighbor holes *p*, *q*, and *r*. (b) A three dimensional representation of the boron atom environment in (a). (c) A representation of the structure of the boride MB_2, where all holes are filled and the boron atoms form a hexagonal net within the close-packed metal lattice.

TABLE I

METAL-RICH BORIDES: STRUCTURAL ARRANGEMENT OF THE BORON ATOMS

p	*q*	*r*	Boron arrangement	Example of stoichiometry
M	M	M	Isolated atoms	M_3B
M	M	B	Pairs of atoms	M_3B_2
M	B	B	Zigzag chains	MB
B	B	B	Double chains or planar nets	M_3B_4 MB_2

chiometries ranging from M_3B to MB_2 can be generated. The hexagonal network for MB_2 is shown in Fig. 9c. The metal-rich borides are characterized by a strong tendency for B–B interactions even at low boron concentrations. For example, $ZnCo_3B_2$ shows B–B bond formation whereas for analogous carbide structures no C–C bond formation is observed at carbon levels of less than 60 atom percent (*95*). Even in the case of structures containing isolated boron atoms (e.g., M_3B), the borides exhibit differences. In typical interstitital structures containing carbon or nitrogen, the main group atom is often found in an octahedral hole in the metal lattice, whereas a trigonal prismatic environment is by far the most common for boron (*96*).

In the second class of structure, the boron-rich borides contain boron in strongly bonded three-dimensional homonuclear networks with the metal atoms distributed in a second, cubic interpenetrating lattice. This class covers stoichiometries from MB_2 to MB_{12}. Note that the MB_2 stoichiometry, as a member of both classes, contains a hexagonal sheet of catenated boron atoms (Fig. 9c). As the boron content increases, three-dimensional networks appear in the structures with the metal atoms distributed throughout the periodic voids. One now begins to see polyhedral cages similar to those observed for discrete borane cages. For example, MB_6 contains octahedral B_6 cages linked in a three-dimensional cubic lattice, with the M atoms accommodated in the holes between eight boron octahedra. Each metal atom thus has 24 nearest boron neighbors. An equivalent description is as a CsCl lattice, with the chlorine replaced with the boron cages as shown in Fig. 10. One might well expect an MB_4 structure to be intermediate between those of MB_2

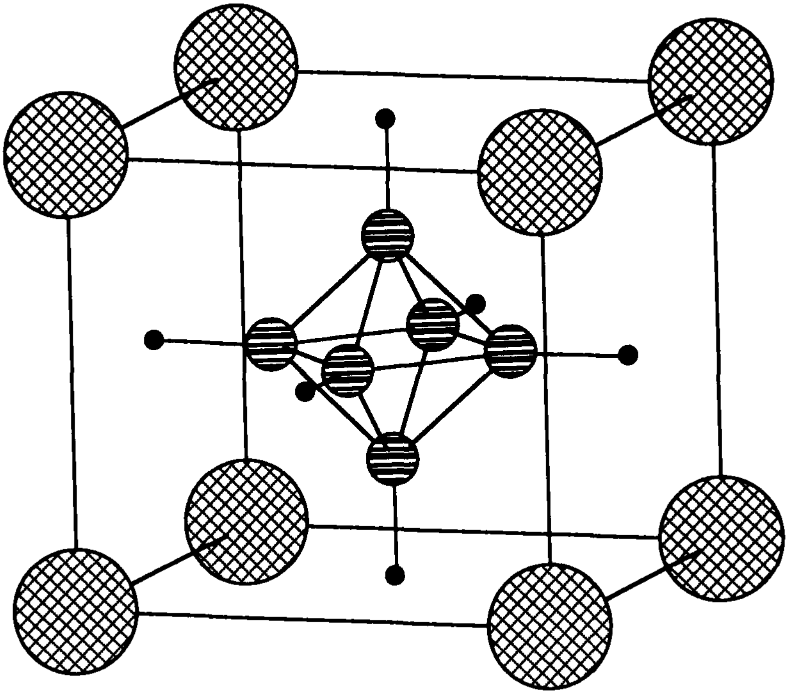

FIG. 10. A sketch of the structure of the boride MB_6, where the large spheres represent metal atoms and the small spheres boron atoms. The dots on lines extending in radial directions from the octahedron of boron atoms represent connections to B_6 octahedra in neighboring cells.

and MB_6. In fact the boron lattice of one MB_4 structure is made up of chains of octahedral B_6 fragments linked radially by B_2 pairs. It should be no surprise then that further increase in boron content leads to boron lattices in which the B_{12} fragment plays a major role. For example, the MB_{12} structure has been described as an NaCl metal lattice with the metal atoms at the Na positions and with each metal atom at the center of a B_{24} cubo-octahedral cage (*97*). The B_{24} cages touch and form a B_{12} cage centered at the Cl positions. Other boron-rich systems contain the B_{12} icosahedron as a principal structural unit, and the structures approach more closely those of elemental boron itself.

The existence of a covalently bonded network should be evident in the energetics of the materials as well as in the geometric structure. Indeed, predictions of heats of formation for boron-rich borides (e.g.,

MB_{12}) using methods successful for alloys are poor, suggesting the existence of a structure-dependent term (*7*).

It is in the boron-rich systems that one can find evidence that the chemistry of the element as expressed in its bonding does not change in going from discrete cages to cages that constitute fragments of an extended network. Lipscomb has effectively reviewed the connections between boron structures in the boranes and borides (*98*). For our purposes the MB_6 borides constitute a good example. In fact, the similarity of the B_6 cage in the solid state to the discrete anion $[B_6H_6]^{2-}$ is even more striking in that the electronic structure of the solid and the group theoretical arguments suggesting a charge of -2 for an octahedral B_6H_6 cage were described nearly simultaneously in insightful papers (*99, 100*). In later work the molecular orbital description of $[B_6H_6]^{2-}$ was further refined and the results have already been given in Fig. 2 (*101, 102*). The preparation and characterization of $[B_6H_6]^{2-}$ followed these studies (*103*). The same was true for $[B_{12}H_{12}]^{2-}$. The solid state evidence for the B_{12} cage was followed by the theoretical prediction of the stability of $[B_{12}H_{12}]^{2-}$, which in turn was followed by preparation of the actual anionic material (*104, 105*). The ultimate distillation of these and subsequent observations into the electron counting rules was sketched in Section II,B.

To make the connection more explicit, the electronic structure of MB_6 in the so-called tight binding approximation is presented in Fig. 11 (*99*). Here the bands for the boron sub-lattice and the molecular orbitals from whence they are derived are divided into exo- and endo-cage types. The endo-cage bonding orbitals (See Section II,B) give rise to three low-energy bands, and the exo-cage orbitals give rise to another. The lowest unfilled band is derived from the t_{2u} symmetry cage antibonding orbitals. There are 18 electrons available per B_6 unit, which is two short of the number required to fill the lowest four bands. However, if the metal formally transfers two electrons to the boron lattice, the four lowest energy bands are completely filled and the material would not be expected to exhibit metallic conductivity. For formally divalent metal atoms with low first and second ionization potentials this is what is observed. If the metal is trivalent it should exhibit metallic conductivity, because an additional electron transferred to the boron lattice will lead to an unfilled band. Alternatively, if the electron remains on the metal it may populate an unfilled band associated with the metal lattice. The question of how many electrons are actually transferred in a boride (and in what direction) is not an easy one to answer and will be discussed further.

The immediate similarity of electron counting in $[B_6H_6]^{2-}$ and MB_6

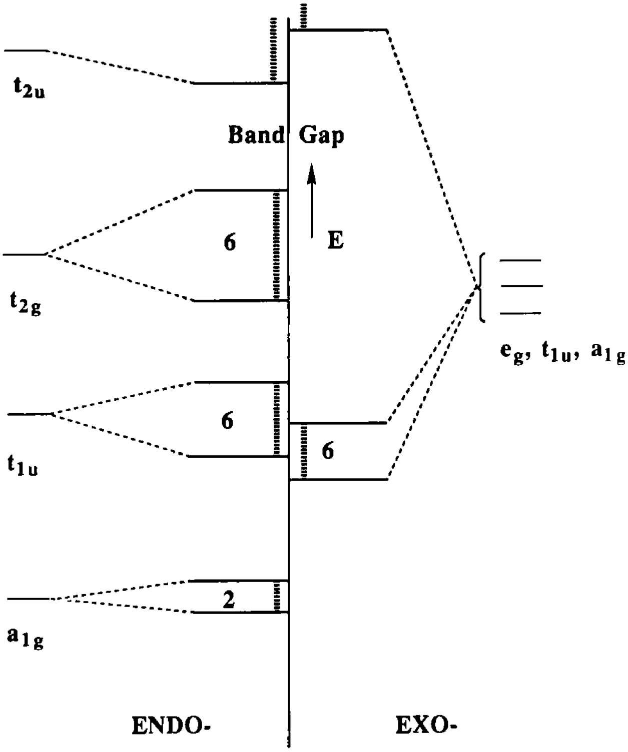

FIG. 11. A qualitative representation of the band structure of a MB_6 boride as derived from the molecular oribtals of isolated B_6 fragments. See Fig. 3 for a representation of the molecular orbitals of the isolated $[B_6H_6]^{2-}$ anion.

suggests that the rules derived for discrete molecular cages might be very useful in analyzing the structure of more complex borides containing cages in the boron lattice. This is in fact the case as shown by a modern example. The boride Li_3B_{14} contains two types of boron cages connected via exo-cage B–B bonds in a three-dimensional network (*106*). These cages are B_8 closo dodecahedral and B_{10} closo hexadecadedral in the ratio of 1:2. The electron counting rules for these closo clusters requires two more electrons per cage to fill the bonding orbitals. Thus $\{[B_8]^{2-}([B_{10}]^{2-})_2\}$ requires six $[Li]^+$ to balance the charge; that is, the stoichiometry is Li_6B_{28} as observed. Note that although the electronic properties of the metal lattice are directly, if not simply, related to atomic properties, the electronic requirements of the boron lattice depend not only on the properties of the boron atom itself but also on the covalent bonding requirements of the network.

As is apparent from the foregoing discussion and contrary to "normal" chemistry, the position of the metal in the periodic table does not correlate closely with observed metal boride stoichiometry. On the other hand, one certainly expects the relative strength of metal–metal bonding to be important in determinining relative stability of structural types and, thus, stoichiometry. There is a "general rule" that main group and *f*-block metals form boron-rich borides and transition metals form metal-rich borides, which reflects the fact that the metal properties are important. Binary transition metal borides have stoichiometries ranging from M_4B to MB_4, with the last having a different structure than that mentioned above. (Further discussion follows.) Borides even richer in the metal fraction are observed for ternary compounds (*95*).

III. Bridging the Molecule–Solid State Interface

We have already indicated a few ways in which information on discrete species leads to a better understanding of solid state metal borides. This is an example of a general theme that has been pursued effectively by others. For example, von Schnering has pointed out the importance of bridging the "unnatural" gap between molecular chemists and solid state chemists and states "for a full understanding of the relationship stoichiometry-structure-properties one needs—after determining the facts—both, the fearless drawing of bond lines *and* the spreading of nets through packed structures." (*107*) In a later review he and Nesper put forth general ideas concerning the aggregation of building units, be they atoms, molecules, clusters, or even blackberries (*108*). The result is a better insight into the organization of crystalline materials of complex structure. Further, calculational approaches led by those of Hoffmann have drawn many ties between the electronic structures of discrete systems and those of related solid state materials (*109, 110, 111*). In this section, some recent results that serve to both strengthen the connection between metallaboranes and metal borides and raise some questions concerning the latter are discussed in the context of the metallic behavior of boron.

A. METAL-RICH METALLABORANES

Recently three discrete transition metal borides have been prepared and structurally characterized. These metal-rich metallaboranes contain boron environments that are formal analogues of the metal borides containing isolated boron atoms. Comparison of some of the structural parameters allows comment on some of the generalizations concerning the solid state compounds.

Two of the known discrete borides are products of cluster expansion reactions carried out on $[HFe_4(CO)_{12}BH]^-$ (*112*). In the first, reaction with sources of $[AuPR_3]^+$ yields $Fe_4(CO)_{12}B(AuPPh_3)_3$ with a cluster core as shown in Fig. 12a (*113*). The butterfly array of iron atoms of the starting material is retained with the gold atoms asymmetrically arranged about the open face, totally enclosing the single boron with metal atoms. In solution, the phosphine ligands on the gold atoms are equivalent, and the CO ligands on the "wing-tip" and "hinge" iron atoms are pairwise equivalent. Hence the solid state structure, insofar as the gold atoms are concerned, must not be a rigid one. The second discrete boride, $[Rh_2Fe_4(CO)_{16}B]^-$, forms from the reaction of $[HFe_4(CO)_{12}BH]^-$ with $[Rh(CO)_2Cl]_2$ (*114*). The core structure of this compound, shown in Fig. 12b, is a slightly distorted octahedron containing the metal atoms. In contrast to the boride containing gold atoms,

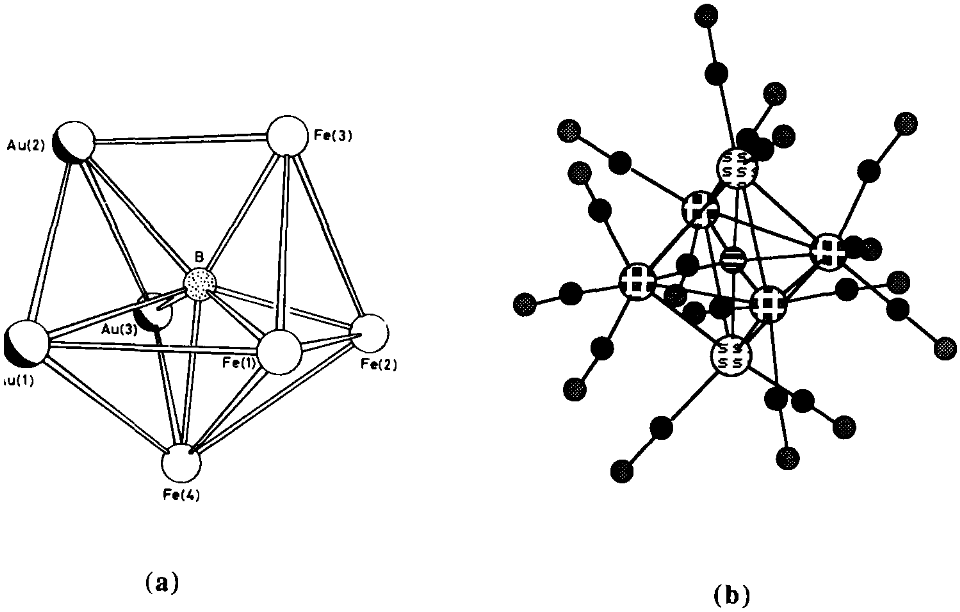

FIG. 12. (a) The structure of the cluster core of $Fe_4(CO)_{12}(Au_3PPh_3)_3$. [Reprinted with permission from Harpp, K. S., Housecroft, C. E., Rheingold, A. L., and Shonge, M. S., *J. Chem. Soc., Chem. Commun.* 965 (1988). Copyright 1988 by The Royal Society of Chemistry.] (b) The structure of $[Rh_2Fe_4(CO)_{16}B]^-$.

the butterfly structure of the starting material has now been lost and the rhodium atoms are found in trans positions. However, spectroscopic evidence shows the initial formation of the cis isomer containing the iron atoms in a butterfly array. Rearrangement occurs readily at ambient temperature. Finally, the third example of a boride, $HRu_6(CO)_{17}B$, is isolated from the reaction of $Ru_3(CO)_{12}$ with diborane, and the cluster core is analogous to that of $Ru_6(CO)_{17}C$ (*115*). This compound contains a hydride, but it is bound to the metal framework rather than to the boron atom. In the homonuclear metal cluster the boron atom is again found in an octahedral environment of six metal atoms.

In the metal-rich solid state borides there are a number of compounds with isolated boron atoms. However, with few exceptions, the distribution of metal atoms around the boron is trigonal prismatic, cubic antiprismatic, or tetrahedral rather than an octahedral (*116*). This observation has often been discussed in the past on the basis of the radius ratio rule; that is, r_B/r_m exceeds 0.414, the value most favored for the octahedron (*95*). Using a radius for boron of 0.88 Å the calculated ratios for typical borides (e.g., Re_3B) range from 0.64 to 0.71 Å, thereby substantially exceeding the radius ratios for both octahedral and trigonal primatic (0.528) arrangements. In the characterized discrete boride, $[Rh_2Fe_4(CO)_{16}B]^-$, the metal–metal distances are typical of those for species with direct bonding. From this structure the calculated r_B is 0.67-0.69 Å and the radius ratio is 0.52–0.51, which is much smaller than previously thought. Hence, in the discrete octahedral case there appear to be no restraints caused by the requirements of metal–metal bonding. It seems unlikely that it is size alone that lies behind the trigonal prismatic geometry in the solid state. The difference between the geometries of discrete and solid state borides may result from the fact that the exo-cluster connections are very different. In the former, connections are to CO ligands whereas in the latter they are to additional metal atoms. Two factors may be important. First, the exo-CO ligands in the discrete clusters induce greater directional character to the metal–metal bonding. Second, the exo-environment affects cluster electron count; for example, adding two more electron pairs via two additional exo ligands can result in an octahedral interstitial nitride cluster being converted to a trigonal prismatic cluster (*117*). It is also possible that weak B–B interactions are in fact important in determining the metal environment of the boron atoms in the solid state. For example, even in Rh_5B_4 which contains boron atoms in octahedral holes in a close-packed metal lattice, "strings" of four boron atoms (B–B distance of 2.22 Å) separated by 3.306 Å are observed (*118*). The B–B bonding is considered “doubtful” but the chains are still considered elements of the structure.

Charge transfer between bonded atoms is a fundamental characteristic of the nature of the bond. Thus, it is not surprising that it has received considerable attention in the case of the borides (*119*). Two types of behavior are advocated. In metal-rich borides, electron transfer from boron to the metal *d*-band is suggested, whereas for boron-rich borides with extensive covalent B–B bonding the metal atoms transfer electron density to the boron network. A number of arguments are put forward in support of this generalization, which, in the case of the metal-rich borides, seems to go contrary to the relative electronegativities of boron and the metals. For example, the situation for MB_6 was discussed above where it was pointed out that the requirements of the boron network is the principal driving force for electron transfer from the metal to boron. In the case of metal-rich borides the direction of electron transfer is based on the interpretation of a variety of physical experiments (e.g., Mössbauer measurements (*120*). Although they are reasonable it is difficult to see that the interpretations of these indirect experiments are unique.

Recent contributions to this discussion lead one to doubt the validity of the generalization concerning direction of charge transfer in metal borides. In fact there can be no simple rule of this type. Calculations on the electronic structure of transition metal borides MB_2 with the AlB_2 structure demonstrate that the charge on boron depends on the electron count, which varies with the identity of M (*121*). In those borides that are intermediate between metal-rich and boron-rich borides, boron charge varies from $+0.8$ to -0.4 in going through the series Ca, Sc, Ti, V, Cr, Mn, Fe, Co, and Ni calculated for the structure of TiB_2. For iron the charge is 0.0. Further, tight binding calculations on MB_4 borides and related systems have demonstrated that, contrary to the general rule, charge transfer from the boron network to the metal lattice is probable (*122*). Calculations for M = V, Cr, Mn, Fe, and Co yield charges at boron of $+0.47$, $+0.37$, $+0.28$, $+0.12$, and -0.06, respectively. Note that the increasing charge on boron follows metal electron count, not relative electronegativity difference. Only the Cr and Mn derivatives are known, consistent with the suggestion that the “tetragonal” net should be increasingly unstable with increasing electron count (*123, 124*). Clearly, it is the requirements of this network relative to those of the metal that are important. That is, the apparent instability of the squares in the structure is reduced by an appropriate metal electron count and low electron density on boron.

Second, band structure calculations on TiB, MnB, FeB, and CoB yield low energy, wide bands that are B–B and B–M bonding and flat, higher energy bonds derived mainly from the metal 3*d* orbitals. In going from Ti to Co the energy of the Fermi level falls from −5.7 to −9.3 eV. The charges on the metals are +1.31, +0.62, +0.30, and 0.00 for Ti, Mn, Fe, and Co, respectively. Absolute charges are sensitive to choice of basis functions, but the results still suggest that Pauling may not have been wrong in suggesting metal-to-boron electron transfer for the compounds with isolated or nearly isolated boron atoms (*125*).

In addition, the information gained from the discrete analogues of the solid state borides provides a new view of this question. Fenske–Hall nonparameterized calculations on monoboron metallaboranes containing different numbers of direct metal–boron interactions show a monotonically increasing negative charge on the boron as the number of metal–boron interactions increases (*126*). Similar calculations on $[Rh_2Fe_4(CO)_{16}B]^-$ yields the highest Mulliken charge we have ever calculated for a metallaborane (*127*). It is clear that in the discrete boride cluster the electronegativity difference is a strong factor in favor of metal-to-boron electron transfer and that the net transfer to boron increases as the number of metal-boron interactions increase. This occurs even though a ML_x fragment with strong π acceptor ligands (e.g., L = CO) can behave as though quite electronegative, thereby lending Brönsted acidic character to metal carbonyl hydrides (*128*). In addition, interstitial metal hydrides formed from the less electronegative metals behave as hydrides in a chemical sense (*129*). Thus, if boron-to-metal charge transfer occurs for the solid state metal borides with isolated boron atoms, it must be due to an electronic demand created by the metal lattice.

B. TRANSITION TO THE SOLID STATE

We have seen how bonding principles carry over from discrete species to related fragments in the solid state. An interesting question then is whether the same discrete species can serve as precursors for the efficient production of specific solid state materials containing the cluster cores of the discrete compounds as building blocks of the solid.

Metal organic chemical vapor deposition (MOCVD) is a well-established, practical technique for forming simple as well as complex solid state films (*130*). For binary systems the conventional approach is to use mixtures of the most readily available molecules containing the elements of interest. This approach has been employed to prepare borides of several types. For example, iron–boron alloys have been prepared with 9–13% Fe (*131*), and $FeB_{29.5}$ has been made directly from β-rhombohedral boron and iron metal (*132*). However, the reagents used in this approach are difficult to activate and require rigorous conditions for deposition. This leads to restrictions in the substrates that can be utilized and, in the case of thermal activation, often results only in the formation of the most stable form of the solid.

In recent years a number of groups have developed compounds that serve as single precursors for specific binary materials (*133, 134, 135, 136, 137, 138, 139, 140, 141, 142*). In this approach, the objective is to synthesize precursor molecules that are easy to handle with low toxicity and that intrinsically contain not only the desired stoichiometry of the material but also a low energy decomposition pathway. When successful these rational precursors have the desired properties of convenience and safety but, as important, create opportunities for preparing films of presently known stoichiometry with new properties as well as for exploring systems of unknown stoichiometry and properties.

Three groups have reported an MOCVD approach to the preparation of metal boride films. In one, $Ti(BH_4)_3(dme)$, dme is $(1,2\text{-}(MeO)_2C_2H_4)$, was used to deposit pure, amorphous, thin films of TiB_2 on pyrex substrates under mild conditions (*143*). The films were pure, showing neither titanium metal or elemental boron, and other impurities such as oxygen were low. Films of ZrB_2 and HfB_2 were made in an analogous fashion. In a closely related study, films of ZrB_2 and HfB_2 were prepared from the boron hydrides and characterized (*144*). Recently a variety of approaches for the synthesis of ZrB_2 from $Zr(BH_4)_4$ were explored (*145*). These authors report films formed at higher temperatures contained excess boron, while those at lower temperatures were boron deficient.

Our synthetic chemistry led us to consider $HFe_4(CO)_{12}BH_2$ as a potential source of the well-known metallic glass $Fe_{80}B_{20}$ (METGLAS) (*146*); that is, as illustrated in Fig. 13, $HFe_4(CO)_{12}BH_2$ contains a possible building block of the $Fe_{80}B_{20}$ material coordinated to CO and H ligands (*147*). This compound was an ideal starting point for testing such an approach, as the properties of $Fe_{80}B_{20}$ have been thoroughly defined in the literature (*148*). Hence product characterization was simplified and unusual properties due to the method of preparation, if any, could be easily recognized.

Preliminary experiments showed that $HFe_4(CO)_{12}BH_2$ decomposed under thermolytic conditions to yield CO and H_2 plus a residual solid containing boron and iron (*149*). In more recent studies films were prepared by subliming $HFe_4(CO)_{12}BH_2$ in a low-pressure (base pressure 10^{-8} torr, deposition pressure 10^{-4} torr) MOCVD reactor of our own design on substrates resistively heated to 180°C. Uniform, contigu-

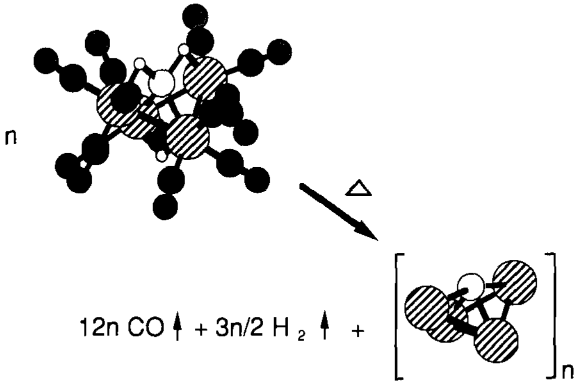

FIG. 13. Schematic drawing of the conversion of $HFe_4(CO)_{12}BH_2$ to the amorphous alloy $Fe_{80}B_{20}$ by loss of CO and H_2.

ous films of 1000 Å in thickness with a metallic luster were grown in ca. 30 m on glass, silicon, and metal substrates. The films adhere well to all substrates examined and were amorphous to X-rays. Analysis by Auger and XPS showed a Fe : B ratio of 4 : 1 and no impurities other than carbon and oxygen ($< 5\%$). The chemical environment of the boron atom as measured by the 1*s* binding energy is identical to that of the authentic material. Mössbauer spectroscopy demonstrates a distribution of hyperfine fields typical of the authentic amorphous metal. Resistivity measurements yield values two times larger than those of the bulk materials. These results unambiguously define $HFe_4(CO)_{12}BH_2$ as a useful single precursor for the production of thin films of an authentic metallic glass under mild conditions.

From the discussion in Section II,C it should be clear that there is a relationship between the structures of borides and boranes as far as the boron networks are concerned. A comparison of the literature shows that the known structural diversity of the boranes is much greater than that of the borides. This may well be due to the rigorous conditions required for boride preparation; that is, only the most stable boron networks are formed. The low-temperature routes illustrated in the foregoing work suggest an approach to presently unknown compounds with novel boride networks. Hence, the multitude of known metallaboranes constitute a stockpile of potential precursors to metal borides with new and perhaps useful properties.

ACKNOWLEDGMENTS

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