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Molecular Models of Solid State Metal Boride Structures

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Based on existing connections between borane cages and boron-rich metal borides on the one hand and metal clusters containing boron atoms and metal-rich borides on the other, selected metallaboranes of intermediate stoichiometry are investigated as models for transition metal borides with similar M/B ratios. This study is possible due to the recent development of a general route to metallaboranes for group 5–9 metals that permits the distinct role of the transition metal in metallaborane cluster bonding to be revealed. The comparison shows that it is MM and MB covalent bonding rather than M and B electronic charges that drives change in structure with metal identity. © 2000 Academic Press

INTRODUCTION

In the words of Von Schnering (1) an "unnatural gap" exists between molecular chemists and solid state chemists that must be bridged in order to achieve "a full understanding of the relationship stoichiometry–structure–properties." Interestingly, this bridge was established for boranes and boron-rich metal borides more than a decade before his article was written when it was recognized, first in the solid state and then for molecular species, that, e.g., an octahedral cage formed of six BR fragments required an overall charge of 2-. Thus, we have CaB_6 formulated as a zintl phase $[Ca^{2+}][B_6^{2-}]$ with a three-dimensional network of octahedral B_6 cages (2) to compare with discrete $[B_6H_6^{2-}]$ ions (3). The seven skeletal electron pairs seen to be associated with cage bonding in each example of a six-vertex deltahedron (octahedron) became a key fact supporting the cluster electron counting rules of Wade and Mingos (4–8).

Metal-rich borides are characterized by metal lattices containing isolated boron atoms in interstitial holes with a building block motif often consisting of a tricapped trigonal prism (Fig. 1) (9, 10). Subsequently, transition metal clusters containing interstitial boron atoms were characterized. Most possess octahedral shapes (11) but a couple exhibit trigonal prismatic shapes and serve as models for the local bonding environment of the boron atom in solids. One in particular, $[HFe_7(CO)_{20}B]^{2-}$ (12), serves as an excellent local bonding model for the solid boride Fe_3B (Fig. 1) (13). Early considerations of bonding focused on charge transfer either metal to boron (zintl model) or boron to metal (9). However, it is clear for the molecular cluster mimics that both MM and MB bonding are important (14).

One of the benefits of cluster model compounds is that spectroscopic properties are more easily measured and interpreted in terms of bonding models. For example, the ^{11}B NMR chemical shifts of interstitial boron atoms exhibit the largest positive values observed for diamagnetic boron compounds. We have argued (15) that this is not associated with the charge on boron but rather results from the strong interaction of the B_{2p} orbitals with metal cluster orbitals of suitable symmetry. This not only generates a set of filled, strongly MB bonding orbitals but also a low-lying set of unfilled orbitals with significant B_{2p} character. The latter accounts nicely for the large downfield shifts observed for the boron resonances. In recent years, similar shifts have been observed for solid state compounds containing boron in interstitial sites, e.g., $Rb_5Zr_6Cl_{18}B$ (16), thereby reinforcing the connection between molecular and solid state compounds.

The purpose of this work is to demonstrate that model compounds now exist that mimic some of the bonding properties of metal borides of intermediate composition involving the transition metals, i.e., the metal does not simply serve as a negative charge donor as in a zintl phase. Two developments permit this discussion. The first is the ability to synthesize metallaboranes containing a range of metal atom types with comparable numbers of metal and boron atoms in the core. The second is the firm establishment of cluster electron counting rules which then provide a baseline against which unusual metal effects can be evaluated.

A GENERAL SYNTHESIS OF METALLABORANES

In work published over the past five years or so, we have established a general route to metallaboranes of the type $(Cp^*M)_nB_xH_y$, where $Cp^* = \eta^5\text{-}C_5Me_5$ and $n = 1\text{–}3$ and $x = 2\text{–}5$, via the reaction of monocyclopentadienyl metal

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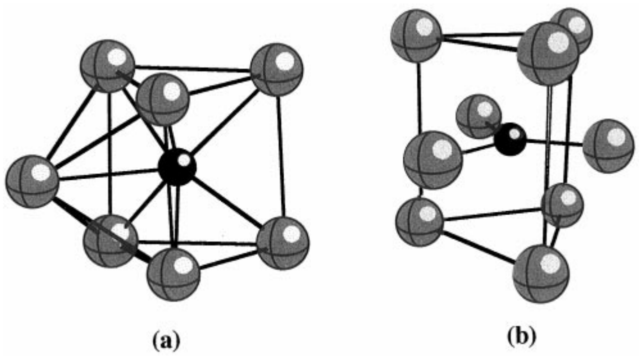

FIG. 1. (a) Core structure of $[HFe_7(CO)_{20}B]^{2-}$ vs (b) the building block of solid Fe_3B.

halides with monoboranes (17–22). Although the reaction of metal chlorides with borohydride is a known method for the production of hydrides (and reduction of the metal center), what has not been appreciated is the fact that conversion of a polychloride to a polyborohydride permits H_2 elimination with the formation of BB and MB bonds to be competitive with loss of borane to form a polyhydride. It was the work of Ting and Messerle (23), that demonstrated this unambiguously for the first time. In contrast, something unanticipated before our work is the fact that BH_3THF readily reacts with the same substrates to form metallaboranes with the chlorine being eliminated as BH_2Cl in all cases except one.

For borohydride, the number of boron atoms in the final product is limited by the number of Cl atoms in the substrate. However, with BH_3THF cluster expansion can continue after all the Cl atoms on the metal are consumed. Indeed we have unambiguously demonstrated this for Rh, Ru, and Cr taking a M_2B_n cage from $n = 2$ to 3, $n = 3$ to 4, and $n = 4$ to 5, respectively (21, 24). These differences allow some selectivity in the synthetic reaction. Thus, for example, the ultimate product in the reaction of $[Cp^*MoCl_2]_2$ with BH_4^- is $[Cp^*Mo(B_2H_6)]_2$, whereas with BH_3THF it is $Cp^*_2Mo_2B_5H_9$ (19). Additional complexity occurs when reduction is competitive with metallaborane formation. Cp^*MoCl_4 reacts with BH_4^- to give $[Cp^*Mo(B_2H_6)]_2$ via $[Cp^*MoCl_2]_2$ (19). On the other hand, Cp^*WCl_4 reacts with excess BH_4^- to give $Cp^*WH_3B_4H_8$ while less than stoichiometric quantities yield reduction to $[Cp^*WCl_2]_2$ (20).

To date, more than 25 metallaboranes containing metals from groups 5–9 have been synthesized in our laboratory in Schlenk systems, using commercially available solutions of $LiBH_4$ and BH_3THF and syringe techniques. In some cases the monocyclopentadienyl metal halides can also be purchased. Isolated yields of crystalline materials range from ≈30% to quantitative. Generally the structures obey the electron counting rules (6, 8), albeit notable exceptions have been discussed elsewhere (25, 26). Taking into account derivative reactions, e.g., cluster expansion with metal or borane fragments, a significant set of compounds exists and can be used for the purpose set forth above.

METAL BORIDES OF INTERMEDIATE COMPOSITION

As with metal-rich borides, the question of direction and extent of charge transfer constituted the focus of early discussions of bonding. Recent theoretical studies, however, put more emphasis on the dominant role of interatomic covalent bonding. Thus, Burdett and co-workers have noted in two insightful studies of MB_2 and MB_4 borides a correlation between the filling of bands of MM and MB antibonding character and changes in properties and structures (27, 28). Thus, as shown schematically in Fig. 2 for the MB_2 system, there is a change in structure as one moves toward more electron-rich metals from the AlB_2 type (fully stuffed

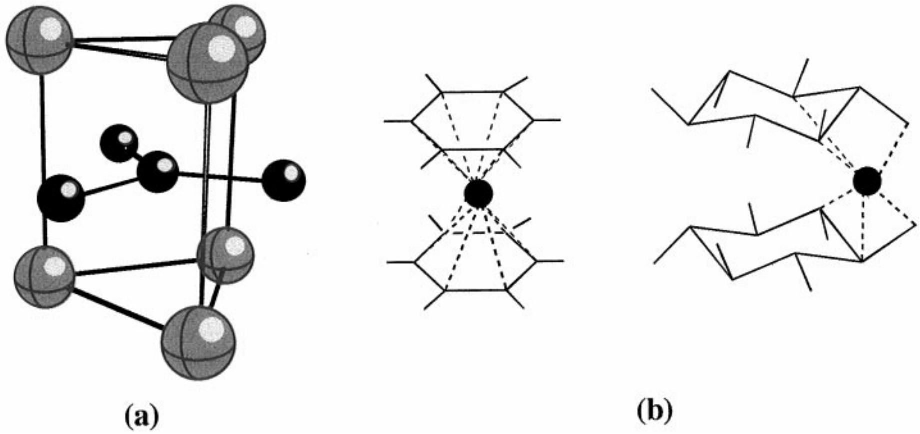

FIG. 2. (a) The building block of MB_2 borides with the AlB_2 structure. (b) Schematic representation of the structural change occurring in going from, e.g., CrB_2 (AlB_2 structure) to that of ReB_2.

graphite structure) to a version that contains puckered or corrugated boron sheets. In doing so, the metal atom coordination number decreases and the extent of *MM* and *M*B bonding decreases.

As far as charge transfer goes, the calculated charge on boron varies from 0.6 for Sc to -0.4 for Ni. This is exactly opposite to what one would expect if the graphite-like boron lattice for the earlier metals is viewed as $(B^-)_n$—isolelectronic to graphite. On the other hand, the loss of *MM* bonding between the metal sheets correlates nicely with the population of a band of largely intersheet *MM* antibonding character, and it is this that is suggested as the origin of the change in structure for the more electron-rich metals.

One attractive feature of this solid state system is that one sees a change in structure and properties at constant stoichiometry, thereby clearly defining the role of the metal atom. Theory then allows the series to be extended to all the transition metals. The set of metallaboranes described above now allows a similar analysis to be carried out with the added advantage of firm knowledge of the expected structure for a given Wade electron count. The existence of a correlation between structure and bonding for boron-rich and metal-rich borides implies the same should be true for compounds of intermediate stoichiometry. Using the MB_2 borides as a guide suggests that as the metal group number increases, there will be a tendency for metal coordination number and *MM* and *M*B bonding to decrease. Is it possible to discover corroboration in an examination of metallaboranes?

HIGHLY CONDENSED METALLABORANES

A considerable amount of published work has established the validity of the electron counting rules for the vast majority of metallaboranes containing group 8 $M(CO)_3$ and group 9 Cp*M* fragments (11, 29–32). Further, the causes of deviations from the electron counting rules due to symmetry are understood (33). The question addressed in this section is the nature of the structural response of a known (or reasonable) closo metallaborane containing one or more Cp*M* fragments when the metal atom is changed to an earlier transition metal. Two examples follow.

The convenient synthesis of $Cp^*WH_3B_4H_8$ in good yield, mentioned above, permitted an examination of its reaction chemistry (34, 35). This tungstaborane obeys the electron counting rules—the three hydrides on tungsten providing the three electrons required to make it analogous to $CpCoB_4H_8$ (36). Hence, we were interested in the consequences of removing one or more of the potentially labile hydrogens. Whatever the initial product, it is not stable and rapidly produces three compounds: $Cp^*{}_2W_2B_5H_9$, $(Cp^*WH)_2B_7H_7$, and $(Cp^*W)_3HB_8H_8$. It is the last two which are of interest here.

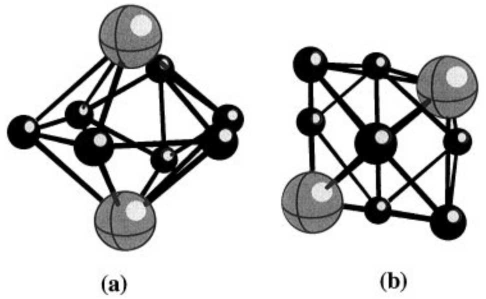

FIG. 3. The observed core structure of (a) $(Cp^*WH)_2B_7H_7$ (and $(Cp^*Re)_2B_7H_7$) compared with (b) a hypothetical $(Cp^*Co)_2B_7H_7$ cluster possessing a distorted tricapped trigonal prismatic geometry.

$(Cp^*WH)_2B_7H_7$ and the isoelectronic and isostructural $(Cp^*Re)_2B_7H_7$ prepared by the cluster expansion reaction of $(Cp^*Re)_2B_4H_8$ with BH_3THF (37, 38) exhibit an unprecedented cluster core geometry for nine-vertex systems. As shown in Fig. 3 the observed geometry can be generated from that of a tricapped trigonal prism (the established structure of a fully closed nine-vertex cluster) by a distortion that converts four five-coordinate vertices into two six and two four-coordinate vertices. Thus, in going from $(Cp^*WH)_2B_7H_7$ or $(Cp^*Re)_2B_7H_7$ to hypothetical closo $(Cp^*Co)_2B_7H_7$ (clusters with threefold axes can possess *n* as well as the normal $n+1$ closo electron pair count (8)), the metal coordination number and the number of *MM* and *M*B bonding interactions decrease.

In Fig. 4 the core structure of $(Cp^*W)_3HB_8H_8$ is compared with that expected for an 11-vertex closed cluster of composition $(Cp^*Co)_3HB_8H_8$ (monometal MB_{10} closo clusters possessing this structure are known for both *n* and $n+1$ electron pair counts (39–41)). The difference between the two cluster structures consists of two diamond–square–diamond rearrangements plus cross cluster WW bonds in $(Cp^*W)_3HB_8H_8$. Thus, in going from $(Cp^*W)_3HB_8H_8$ to hypothetical $(Cp^*Co)_3HB_8H_8$ the metal coordination number and the number of *MM* and *M*B

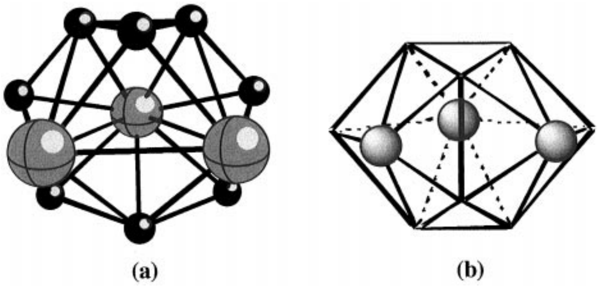

FIG. 4. The observed core structure of (a) $(Cp^*W)_3HB_8H_8$ compared with (b) a hypothetical $(Cp^*Co)_3HB_8H_8$ possessing the geometry known for closo 11-vertex metallaboranes.

bonding interactions decrease just as found in the previous example.

We have discussed elsewhere (35) the connection between these compounds and "hypoelectronic" clusters found in zintl phases (42) as well as those with large transition metal clusters containing close-packed metal atom cores. Essentially, reduction of the metal electron count collapses a closo structure into a highly capped core of lower vertex number. This requires higher metal coordination numbers and an increase in MM and MB bonding interactions. The close connection with the analysis of metal borides summarized in the previous section is self-evident.

SUMMARY

Three molecular examples illustrating the effects of reducing cluster electron count by changing the transition metal while keeping the number of cluster vertices constant have been described. Space does not permit the description of additional examples we have uncovered. However, those considered here are sufficient to demonstrate that as the number of metal electrons available decreases, the cluster adopts a more condensed structure in which the number of MM and MB bonding interactions are increased. The comparison with solid state borides, particularly the description derived from MO analyses, shows close correspondence between the factors that drive structural changes. Thus, it is clear that it is MM and MB covalent bonding rather than M and B electronic charges that dominates change in structure with metal identity in both molecular and solid state borides of transition metals with compositions lying between boron- and metal-rich stoichiometries.

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REFERENCES

1. H. G. Von Schnering, *Angew. Chem. Int. Ed.* **20,** 33 (1981).
2. H. C. Longuet-Higgins and M. D. Roberts, *Proc. R. Soc. London A* **230,** 110 (1955).
3. J. L. Boone, *J. Am. Chem. Soc.* **86,** 5036 (1964).
4. K. Wade, "Electron Deficient Compounds," Nelson, London, 1971.
5. K. Wade, *New Scientist* **62,** 615 (1974).
6. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18,** 1 (1976).
7. D. M. P. Mingos, *Nature* (*London*) **236,** 99 (1972).
8. D. M. P. Mingos and D. J. Wales, "Introduction to Cluster Chemistry," Prentice-Hall, New York, 1990.
9. N. N. Greenwood, R. V. Parish, and P. Thorton, *Q. Rev.* **20,** 441 (1966).
10. T. Lundström, *in* "Boron and Refractory Borides" (V. I. Matkovich, Ed.), Springer-Verlag, Berlin, 1977.
11. C. E. Housecroft, *Adv. Organomet. Chem.* **33,** 1 (1991).
12. A. Bandyopadhyay, M. Shang, C.-S. Jun, and T. P. Fehlner, *Inorg. Chem.* **33,** 3677 (1994).
13. U. Herold and U. Köster, *Z. Metallk.* **69,** 326 (1978).
14. T. P. Fehlner, *Adv. Inorg. Chem.* **35,** 199 (1990).
15. R. Khattar, T. P. Fehlner, and P. T. Czech, *New J. Chem.* **15,** 705 (1991).
16. Y. Tian and T. Hughbanks, *Inorg. Chem.* **34,** 6250 (1995).
17. K. J. Deck, Y. Nishihara, M. Shang, and T. P. Fehlner, *J. Am. Chem. Soc.* **116,** 8408 (1994).
18. Y. Nishihara, K. J. Deck, M. Shang, T. P. Fehlner, B. S. Haggerty, and A. L. Rheingold, *Organometallics* **13,** 4510 (1994).
19. S. Aldridge, M. Shang, and T. P. Fehlner, *J. Am. Chem. Soc.* **120,** 2586 (1998).
20. A. S. Weller, M. Shang, and T. P. Fehlner, *Organometallics* **18,** 53 (1999).
21. X. Lei, M. Shang, and T. P. Fehlner, *J. Am. Chem. Soc.* **121,** 1275 (1999).
22. X. Lei, A. K. Bandyopadhyay, M. Shang, and T. P. Fehlner, *Organometallics* **18,** 2294 (1999).
23. C. Ting and L. Messerle, *J. Am. Chem. Soc.* **111,** 3449 (1989).
24. S. Aldridge, T. P. Fehlner, and M. Shang, *J. Am. Chem. Soc.* **119,** 2339 (1997).
25. T. P. Fehlner, *J. Chem. Soc. Dalton Trans.* 1525 (1998).
26. T. P. Fehlner, *J. Organomet. Chem.* **550,** 21 (1998).
27. J. K. Burdett, E. Canadell, and G. J. Miller, *J. Am. Chem. Soc.* **108,** 6561 (1986).
28. J. K. Burdett and E. Canadell, *Inorg. Chem.* **27,** 4437 (1988).
29. C. E. Housecroft and T. P. Fehlner, *Adv. Organomet. Chem.* **21,** 57 (1982).
30. J. D. Kennedy, *Prog. Inorg. Chem.* **32,** 519 (1984).
31. J. D. Kennedy, *Prog. Inorg. Chem.* **34,** 211 (1986).
32. R. N. Grimes, *in* "Metal Interactions with Boron Clusters" (R. N. Grimes, Ed.), p. 269. Plenum, New York, 1982.
33. D. M. P. Mingos (Ed.), "Structural and Electronic Paradigms in Cluster Chemistry," Vol. 87. Springer-Verlag, Berlin, 1997.
34. A. S. Weller, M. Shang, and T. P. Fehlner, *J. Am. Chem. Soc.* **120,** 8283 (1998).
35. A. S. Weller, M. Shang, and T. P. Fehlner, *Organometallics* **18,** 853 (1999).
36. R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.* **17,** 1522 (1978).
37. A. S. Weller, M. Shang, and T. P. Fehlner, *Chem. Commun.* 1787 (1998).
38. S. Ghosh, unpublished data (1999).
39. J. D. Kennedy, *in* "The Borane, Carborane, Carbocation Continuum" (J. Casanova, Ed.), p. 85. Wiley, New York, 1998.
40. H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* 517 (1986).
41. M. Brown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* 3039 (1990).
42. J. D. Corbett, *Struct. Bonding* **87,** 157 (1997).