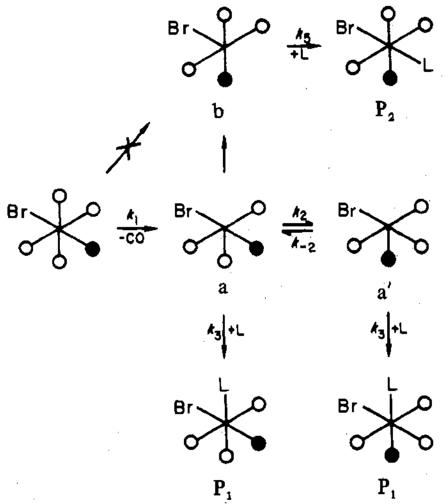
Scheme I[a]



[a] Key: ○, CO originally trans to CO; ●, CO originally trans to Br; L, Lewis base or ^{13}CO.

atoms and substituents and exhibiting differing degrees of substitution is consistent with both ground-state[19,20] and transition-state[21] bonding arguments and is indicative of very significant differences in the free energies of activation for axial vs. equatorial dissociation of carbonyls.[22]

Also note values of $\Delta G^\ddagger$ and $\Delta(\Delta G^\ddagger)$ for combination of nucleophiles with various five-coordinate species (Table II). The values of the latter for a given combination are in the range $0 < \Delta(\Delta G^\ddagger) < 2$ kcal/mol, too small to redirect the stereochemical path of the reaction to that governed by k_4, k_5.[27]

Thus in these systems "quasi microscopic reversibility" dictates that, where there is initial M–CO bond breaking trans to CO, a product containing L trans to another L cannot be produced under kinetic control regardless of possible fluxionality of the five-coordinate species. As has been pointed out by Atwood and Brown,[12] however, exceptions may arise where steric crowding at an octahedral face or edge could significantly increase the free energy of combination via k_3 in Scheme I.

These conclusions are consistent with data in Table I. Products in which the incoming nucleophile is trans to CO, expected on the basis of the preferential fission of a M–CO bond trans to CO (axial) rather than to L, are observed in all cases save those in which there are obvious steric impediments to the path dictated by quasi microscopic reversibility, e.g., for *cis*-$Mn(CO)_4Br(PPh_3)$ in its reaction with triisopropyl phosphite, for which there would be severe congestion at an octahedral face.[12,28]

It is not appropriate to give a detailed analysis of the stereochemical consequences of the results here. In the most favorable cases, however,[22] where L is electron releasing relative to CO and poses minimal steric demands, it is highly improbable that an octahedral complex containing more than the minimal number of trans pairs of carbonyls can be prepared under kinetic control. For amines and related ligands, no such complexes are known.

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(22) In the method for determination of the site of initial M–CO bond fission employed by Brown and coworkers, "the calculated (infrared) spectra are essentially insensitive to an increase in the ratio (k_{ax}/k_{eq}) beyond about 10. This ratio might in fact be (and indeed we believe it is) much larger than this".[13]

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(27) Darensbourg and Graves, for related systems, have pointed out that process a → P_2 (see Scheme I) need not involve the formation of discrete b intermediates and may, in fact, be concerted (D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, **18**, 1257 (1979)). Such a concerted process would involve a high degree of reorganization and, by Hammond's postulate, would be expected to be energetically unfavorable relative to that governed by k_3.

(28) It is reasonable to presume that, where there is crowding at an octahedral edge or face, a trans or *mer* product would be thermodynamically more stable than a cis or *fac* product, as well as being kinetically accessible. Thus, (diphos)$Mo(CO)_4$ reacts with triphenylphosphine to afford *mer*-(diphos)$Mo(CO)_3(PPh_3)$ under thermodynamic control. See also, e.g., E. P. Ross, R. T. Jernigan, and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **33**, 3375 (1971).

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Examples of Possible Polymeric Borane Structures

Sir:

No structural characterization has been made of the intractable polymeric products of pyrolysis of diborane or other boron hydrides. Their approximate composition[1] is $(BH)_x$ where x is a large integer. These polymers can reasonably be expected to bridge the region between small borane molecules and polymeric borides and therefore are probably mainly based upon presently known structural features which I now describe.

At least 10 modes of bonding between polyhedral species, or their fragments, can be listed, followed by only one or two examples of each mode: (1) a single bond in[2] $B_{10}H_{16}$, which is a dimer of B_5H_8; (2) a single three-center BHB bond in[3] $B_{20}H_{19}^{3-}$; (3) two BHB bridges, in[3,4] *photo*-$B_{20}H_{18}^{2-}$; (4) one three-center BBB bond, probably in[5] $B_{15}H_{23}$ and in[6,7] μ-$Fe(CO)_4B_7H_{12}^-$; (5) two three-center BBB bonds, in[8,9] $B_{20}H_{18}^{2-}$; (6) one shared atom, known for a metal atom but not boron, in[10] $(\eta^5\text{-}C_5H_5)CoC_2B_8H_{10}CoC_2B_8H_{10}^-$; (7) two shared boron atoms, cis in[11] $B_{14}H_{20}$ and trans in[12] *n*-$B_{18}H_{22}$; (8) three shared

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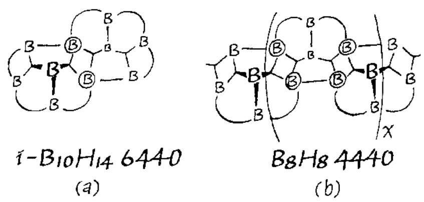

Figure 1. (a) A proposed two-unit conjuncto isomer of $B_{10}H_{14}$. (b) A proposed infinite polymeric structure of composition $(BH)_\infty$.

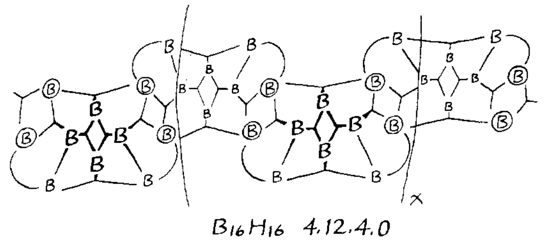

Figure 2. A proposed infinite polymer of composition $(BH)_\infty$ based upon the decaborane(14) formula. Circled boron atoms have no terminal hydrogen atoms attached.

boron atoms, in[13] $B_{20}H_{16}(NCCH_3)_2$ and in[14] α-AlB_{12} and a related structure[15] for boron; (9) four shared boron atoms, in[16] $B_{20}H_{16}$; and (10) a "double cap" join, in[17] $(CH_3)_4C_4B_8H_8FeCo(\eta\text{-}C_5H_5)$. Other multiple, combination, or new modes of joining are probable, as new polyboron systems with other elements, particularly metals, are further explored.

Among both borides and conjuncto boranes, modes 1 and 7, above, are prevalent. Electroneutrality is most easily maintained by joining of nido (or arachno) fragments, rather than polyhedral species whose negative charges can easily be compensated by positive metal ions as in the higher metal borides. Three-dimensional networks can be constructed from, for example, nido boranes by replacing terminal BH bonds by BB bonds to neighboring fragments upon loss of H_2. I wish, however, to direct attention here to the joining by mode 7, in which two boron atoms are shared.

The MgB_4 structure[18] consists of chains of pentagonal pyramids, like those in B_6H_{10} molecules, joined by sharing of two edge boron atoms into an infinite chain in which apexes are alternately up and down. The three-dimensional structure is then formed from interchain BB bonds, which we shall replace by terminal BH bonds (Figure 1). The two-unit structure is an undiscovered isomer of $B_{10}H_{14}$, while the polymeric structure has the composition $(BH)_x$. An analogous structure based upon the known $B_{10}H_{14}$ structure is shown in Figure 2. Here, the two-unit structure is the known[12] *n*-$B_{18}H_{22}$, the predicted three-unit structure is $B_{26}H_{30}$ of *styx* topology 8,18,6,0, and the polymeric structure again has the composition $(BH)_x$. Similarly B_8H_{12} units can be condensed to a two-unit structure $B_{14}H_{18}$ of 6840 topology and a polymeric $(BH)_x$ structure of 2420 topology. Other examples can easily be constructed.

Each condensation involves *formal* loss of B_2H_6 (or two BH_3 units). Hence, the generalization for this mode of fusion is that for large x one formally relates *hypho*-B_nH_{n+8} to $(B_{n-2}H_{n+2})_x$, *arachno*-B_nH_{n+6} to $(B_{n-2}H_n)_x$, *nido*-B_nH_{n+4} to $(B_{n-2}H_{n-2})_x$, and *closo*-B_nH_{n+2} to $(B_nH_{n-4})_x$. Thus only for the nido class does one have $(BH)_x$ in a 1:1 ratio of B and H. However, for large n the distinctions among these classes become smaller. Nevertheless, the nido group may give more highly ordered structures for these polymers. Homogeneity can hardly be expected unless the polymers are formed very slowly from pure starting materials.

Finally, in order not to overemphasize the $(BH)_x$ composition, attention is called to $(B_8H_{10})_x$ which is obtained by pyrolysis of B_8H_{12}.[5] Linkage of B_8H_{10} units by single B–B bonds is only one of the plausible structures for this polymer.

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