Correspondence

Intramolecular Rearrangements in Boron Clusters

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Sir:

Recently,[1] we reported a quite unexpected polytopal isomerism in $B_8H_8^{2-}$ wherein the polytopal form is highly sensitive to environment and stereochemical nonrigidity is anomalously high for a closed-shell cluster aggregate. Specifically, it was found that the $B_8H_8^{2-}$ ion, which in the solid state[2,3] (tetraaminozinc salt), like the isoelectronic carborane[4] $B_6H_6(CCH_3)_2$ and the similar B_8Cl_8[5] molecule (2n framework electrons), has dodecahedral geometry, exists primarily in the square-antiprismatic form in protonic or highly polar media and in the bicapped (square face) trigonal-prismatic form in less polar media *with both forms coexisting in certain nonpolar solvents*. Intramolecular rearrangements occur with facility in both of these solution forms; rearrangement is fast on the nmr time scale at ~30–40° for the bicapped trigonal-prismatic form.[1] It has also been noted[2] that the esr spectrum of $B_8H_8^-$ *may* be interpreted in terms of a highly fluxional structure for this ion radical. This behavior for 8-atom boron clusters is in sharp contrast to the relatively high structural integrity for boranes and carboranes in the 12-, 10-, 9-, 6-, and 5-atom clusters.[6-9] Only in the 11-atom boron cluster is there evidence of high structural plasticity.[10,11] Because this issue of structural form and rigidity in boron clusters is, in our opinion, of general relevance in inorganic chemistry, *e.g.*, metal clusters and coordination compounds,[6-9,12,13] we wish to address our thoughts to these specific issues and to present new experimental evidence on the 7-, 8-, and 11-atom boron clusters.

Tolpin and Lipscomb[10] have shown that $B_{11}H_{11}^{2-}$ in solution exhibits a single ^{11}B nmr doublet (boron–hydrogen spin–spin coupling) down to −73°, a feature that is patently inconsistent with any rigid 11-atom structure save the absurd possibility of a coplanar 11-atom ring. In fact, all crystallographic data for 11-atom boron clusters define an idealized C_{2v} octadecahedral form; here the data relate to 11-atom carboranes and metallocarboranes.[14,15] We have reexplored the low-temperature nmr domain of $B_{11}H_{11}^{2-}$ at 80.5 MHz with temperature and environment as the variables. Counterions that ranged from sodium to organo cations like tetra-*n*-butylammonium were employed so that solvent medium could be varied from water to water–methanol to tetrahydrofuran to dichloromethane to dichloromethane–toluene. In all cases, the ^{11}B resonance was a single doublet (boron–hydrogen spin–spin coupling) that broadened as the temperature was lowered to regions where solvent viscosity increased markedly. There was no evidence of a limiting slow-exchange spectrum consistent with any rigid, plausible geometry for $B_{11}H_{11}^{2-}$. It is of course possible that the single ^{11}B resonance for $B_{11}H_{11}^{2-}$ is due to accidental degeneracies[16] but we deem this a highly unlikely prospect since other polyhedral ions in which there are environmentally distinguishable sets of boron atoms show relatively large chemical shifts between sets. We believe it is safe to conclude, as was first proposed by Tolpin and Lipscomb,[10] that $B_{11}H_{11}^{2-}$ is subject to a very low-energy internal framework rearrangement.

We fully expected $B_7H_7^{2-}$ to be as soft and pliable an aggregate as $B_8H_8^{2-}$ but found the 7-atom cluster to be relatively rigid and detected no evidence of polytopal isomerism on change of solvent or counterion. For $Cs_2^+(B_7H_7^{2-})$ in water, the ^{11}B nmr spectrum at 80.5 MHz consists of two doublets of relative intensities 5 and 2 which is fully consistent with an expected fully triangulated polyhedron, the pentagonal bipyramid.[2] Variation of counterion (Cs^+, Na^+, $(n\text{-}C_4H_9)_4N^+$, and $(C_6H_5)_3PCH_3^+$) and solvent (water, methanol, tetrahydrofuran, *sym*-tetrachloroethane, acetone, acetonitrile, and dichloromethane) gave no evidence of any polytopal form other than the pentagonal bipyramid. For $[(C_6H_5)_3PCH_3^+]_2(B_7H_7^{2-})$ in *sym*-tetrachloroethane, the ^{11}B spectrum at 90° was only consistent with pentagonal-bipyramidal form and there was no evidence of exchange broadening. A distinctive feature of $B_7H_7^{2-}$ ^{11}B spectra was the sensitivity of equatorial boron atoms' relaxation time to medium effects. In water, methanol, and acetonitrile, the two ^{11}B doublets are sharp. Temperature decrease, for example, in the methanol solution of $[(n\text{-}C_4H_9)_4N^+]_2(B_7H_7^{2-})$, led to broadening of both doublets, presumably reflecting viscosity effects, although there was a pronounced differential broadening phenomenon. At −35° the equatorial boron set produced a broad singlet while the axial set yielded a slightly broadened doublet. The differential effect was far more pronounced in solvents of low dielectric constants and polarity; in *sym*-tetrachloroethane $[(C_6H_5)_3PCH^+]_2(B_7H_7^{2-})$ produced a fairly sharp single equatorial resonance and a sharp axial doublet at 90°. Slight puckering of the equatorial girdle and relatively fast pseudorotation are expected[2] phenomena in $B_7H_7^{2-}$ but the nmr line shape changes are probably not due to a pseudorotation process. The extreme variability in the temperature at which doublet broadening occurs with change in the character of the solvent does not bespeak an intramolecular rearrangement process.

The salient issue in boron cluster rearrangements is the genesis of the strikingly low barrier in $B_8H_8^{2-}$, ~12 kcal/mol for the C_{2v} form, and in $B_{11}H_{11}^{2-}$. A clearly distinctive feature in $B_8H_8^{2-}$ is the very small energy differentiation (<12 kcal/mol) among the C_{2v}, D_{2d}, and D_{4d} solution state forms as incisively demonstrated[1,8] in the ^{11}B dnmr study of various $B_8H_8^{2-}$ salts. This satisfies one necessary condition for a low barrier. The second (dynamic) condition is also satisfied, *i.e.*, motions of quite low magnitude are sufficient to describe the reaction cycle

$$\begin{tikzcd}[column sep=small, row sep=small] & C_{2v} \arrow[dl, shift left, harpoon] \arrow[dr, shift left, harpoon] & \\ D_{2d} \arrow[ur, shift left, harpoon] \arrow[rr, shift left, harpoon] & & D_{4d} \arrow[ul, shift left, harpoon] \arrow[ll, shift left, harpoon] \end{tikzcd}$$

Especially notable here are the very small motions involved in the $C_{2v} \rightleftharpoons D_{4d}$ and $C_{2v} \rightleftharpoons D_{2d}$ interconversions.[1,8,17] These motions are definitely smaller than those required for any rearrangement in D_{5h} $B_7H_7^{2-}$, *e.g.*, $D_{5h} \rightleftharpoons C_{2v}$ (monocapped trigonal prism) or $D_{5h} \rightleftharpoons C_{3v}$ (monocapped octahedron). Furthermore, the insensitivity of the ^{11}B nmr of $B_7H_7^{2-}$ to environment suggests that the energy difference between D_{5h} and alternative polytopal forms is larger than the differences among $B_8H_8^{2-}$ forms. Stereochemical nonrigidity is a reasonable expectation for an 11-atom cluster as is implicated[10,11] for the $B_{11}H_{11}^{2-}$ and $B_{10}CH_{11}^-$ polyhedral ions. There is no geometrical construct so well defined that it would represent a deep minimum on the potential energy surface of the 11-atom cluster. As in the B_8 case, the conditions of a small energy difference between plausible idealized structural forms (C_{2v} and C_s) and small rearrangement motions, as in the $C_{2v} \rightleftharpoons C_s$ path,[7,10,18] appear to be satisfied. Detailed discussion, accompanied by full pictorial representations, of the physical features of idealized rearrangements may be found in earlier articles.[1,6-8,17]

Comparison of stereochemical nonrigidity in 8- and 9-atom boron clusters is quite illuminating. If the motions required for interconversion of idealized forms in $B_8H_8^{2-}$ are compared with those in $B_9H_9^{2-}$ for D_{3h} (symmetrical tricapped trigonal prism) $\rightleftharpoons$ C_{4v} (capped square antiprism), there is little substantive difference; if anything, the requisite motions are smaller in the latter case. Yet the barrier to rearrangement in $B_9H_9^{2-}$ must be substantially larger than in $B_8H_8^{2-}$ since the characteristic ^{11}B resonance for D_{3h} $B_9H_9^{2-}$ is observed up to temperatures of 200°.[19] We conclude that in the B_9 case that there is an electronic factor operative in raising the rearrangement barrier; the C_{4v} (capped square antiprism) form, which is the most logical reaction intermediate or transition state, is degenerate[20] for $B_9H_9^{2-}$ making the $D_{3h} \rightleftharpoons C_{4v}$ cycle spin disallowed. (We have no way in which to assess how high in energy the corresponding spin singlet state in C_{4v} symmetry may be but this state need be only ~8 kcal/mol higher to account for the different nmr behavior for $B_8H_8^{2-}$ and $B_9H_9^{2-}$.) This feature *may* largely account for the substantially higher rearrangement barrier in $B_9H_9^{2-}$ than in $B_8H_8^{2-}$ where all plausible intermediates are nondegenerate.[2]

We restate our convictions[6-9] that these data on polytopal form and isomerism in boron clusters relate in a reasonable fashion to the analogous *x*-atom coordination complexes. Rearrangement barriers in eight-coordinate complexes (all ligands identical) should generally be *very* low,[8,21] and if such aggregates are charged, the ground-state form may be very sensitive to environment. The relatively unchartered area of rearrangements in ML_7 and ML_9 complexes should prove rich in stereochemically nonrigid structures. We anticipate that rearrangement barriers in D_{5h} ML_7 complexes will generally be comparable to or slightly higher than for ML_8 species whereas ML_9 barriers should be less than or comparable to those for ML_8 unless, as in $B_9H_9^{2-}$, electronic features proscribe a low-energy rearrangement itinerary.

The polyhedral borane anions, $B_nH_n^{2-}$, are ideal probes for delineation of cluster rearrangement barriers in the comparison with coordination compounds or metal clusters of the form ML_n or M_nL_m. This is especially true where the preferred coordination polyhedron is not a regular polyhedron. Rearrangement barriers for carboranes or any heteroborane cannot be used for normalization procedures since electronic features may obscure intrinsic *x*-atom cluster rearrangement features; the heteroatom residing in a unique position of an irregular polyhedron may substantially raise or lower the rearrangement barrier. In this context, we note that our nmr studies of the $B_6C_2H_8$ carborane system reveal none of the striking fluxional features of the parent $B_8H_8^{2-}$ ion. The carborane $B_6H_6(CCH_3)_2$, like $B_8H_8^{2-}$ in the $Zn(NH_3)_4^{2+}$ salt, is dodecahedral in the solid state.[4] However, ^{11}B nmr studies of this carborane show only two of three required boron atom environments for the dodecahedral form.[22] New and extensive ^{11}B nmr experiments of $B_6C_2H_8$ in various solvents, including CS_2, acetone, and $CHCl_2F$, to temperatures as low as −140° and of *C,C'*-$B_6H_6(CCH_3)_2$ to −140° have shown no indication of the requisite three environmental sets of boron atoms (only two are discerned). These data are consistent with a relatively nonfluxional molecule with accidental equivalence of two sets[22] or a rapid Hoard–Silverton[8,23] rearrangement which equilibrates square-antiprismatic and dodecahedral forms and on the average[8] yields two boron atom environments. The experimental data do not provide a basis for selection of alternatives.[24]

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Registry No. $B_8H_8^{2-}$, 12430-13-6; $B_{11}H_{11}^{2-}$, 12430-44-3; $B_7H_7^{2-}$, 12430-07-8.

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Mechanism for the Olefin Metathesis Reaction

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Sir:

One of the more remarkable catalytic reactions is olefin metathesis[1] (1) in which the net transformation comprises

$$RHC{=}CHR' \rightleftharpoons RHC{=}CHR + R'HC{=}CHR' \qquad (1)$$

scission of a carbon–carbon double bond. With appropriate catalysts, this reaction is very fast at 25° with equilibrium attained in 1–3 min. The reaction mechanism is as yet unestablished, and an understanding of this profound C=C bond breaking-making reaction remains a major scientific challenge. I wish to present here a simple metathesis reaction scheme based on metal–carbene intermediates. This scheme applies principally to the metathesis[2,3] catalyzed by the products from the interaction of tungsten(VI) chloride and alkylating (or reducing) reagents.

We have found that tungsten(VI) chloride, dissolved in benzene, reacts with metal alkyls at 25° with evolution of alkanes and small amounts of alkenes.[5,6] Especially instructive is the reaction course of dimethylzinc with tungsten(VI) chloride in benzene (presence or absence of olefin). Methane