Selective Synthesis of the Nonachlorononaborate Clusters B_9Cl_9 and $B_9Cl_9^{2-}$

By RAIFAH M. KABBANI and EDWARD H. WONG*
(*Department of Chemistry, Fordham University, Bronx, New York* 10458)

Summary The redox relationship between dianionic and neutral boron clusters is demonstrated by the oxidation–chlorination of nonahydrononaborate (2−) with sulphuryl chloride to give the neutral nonachlorononaborate cluster, and its subsequent reduction back to the dianionic nonachlorononaborate(2−) species.

THE redox reactions between the neutral and dianionic polyhedral boron hydrides and their derivatives can be represented by: $B_nX_n^{2-} \rightleftharpoons (B_nX_n^-) \rightleftharpoons B_nX_n$ (X = H, Cl, or Br; $6 \leqslant n \leqslant 12$). Although they may be possible in some cases,[1] there has as yet been no clear experimental verification of such interconversions. We report here a convenient and selective oxidative synthesis of the neutral B_9Cl_9 cluster using the oxidizing–chlorinating reagent SO_2Cl_2, and demonstrate also its ready reduction to the $B_9Cl_9^{2-}$ species.

When 9 equiv. of SO_2Cl_2 is added under nitrogen to a methylene chloride solution of $[Bu^n_4N]_2[B_9H_9]$ at −78 °C, an instantaneous reaction is observed. Upon warming to room temperature, good yields of $[Bu^n_4N]_2[B_9Cl_9]$ can be isolated.† Addition of excess (20 equiv.) of reagent, however, afforded the neutral B_9Cl_9 cluster in 30—40% yield in addition to $B_9Cl_9^{2-}$. The neutral product is easily isolated by extraction with hexane or sublimation to give pure B_9Cl_9 without contamination from other perchlorinated boron clusters.‡

It has been established that increasing halogen substitution will correspondingly increase the oxidation potential of polyhedral borane dianions.[2] Under these conditions, we have found that neither $B_9Cl_9^{2-}$ nor $B_9Cl_8H^{2-}$ can be readily oxidized to the neutral product. It is reasonable to postulate the initial oxidation of dianions with low degrees of chlorination to give neutral $B_9Cl_xH_{9-x}$

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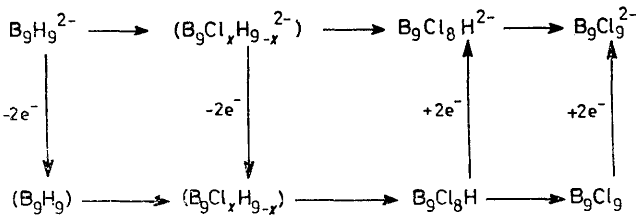
† The $[Bu^n_4N]_2[B_9Cl_9]$ salt was characterized by elemental analysis and spectral data.

‡ B_9Cl_9 was characterized by mass spectral and u.v., and i.r. data and is identical to that prepared by G. F. Lanthier and A. G. Massey, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1807.



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species. These are then rapidly perchlorinated by excess of SO_2Cl_2 to form the B_9Cl_9 product (Scheme). The feasibility of the latter process is illustrated when we found that SO_2Cl_2 does chlorinate B_9Cl_8H to give B_9Cl_9 under similar conditions.[3]

Based on current electron-counting rules,[3] B_9Cl_9 is formally two electrons short of a closed-shell configuration and can thus be expected to undergo ready reductions to give $B_9Cl_9^{2-}$. This is realized when B_9Cl_9 is treated with a methylene chloride solution of Bu^n_4NI and the dianionic $B_9Cl_9^{2-}$ can be isolated in quantitative yields.

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[2] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 159.

[3] B_9Cl_8H and $B_9Cl_8H^{2-}$ were prepared by the method of J. A. Forstner, T. E. Haas, and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 155.

[4] K. Wade, *Chem. Comm.*, 1971, 792; *Inorg. Nuclear Chem. Letters*, 1972, **8**, 823.