termediate (in Scheme I the efficiency of X^- in the competition is measured by the ratio k_{-D}/k_T). Mass law retardation of substitution in a solvento intermediate by the leaving group chloride is well-known in the substitution reactions of *trans*-$[Pt(PEt_3)_2RCl]$ complexes and requires that the product of the rate constant for chloride anation of the solvento complex and the concentration of chloride is comparable in magnitude to the analogous product for the entering nucleophile.[4] It can also be important when there is a fast and reversible solvolysis (as in Scheme II), but the solvento intermediate can offer a favorable pathway for reaction *with a reagent other than the halide ion produced in the solvolysis.* Furthermore addition of Ag^+ to methanolic solutions of the starting complexes produces cis–trans isomerization,[5] instead of inhibiting it through elimination of the halide ion. It is also difficult to understand why Scheme II assumes a facile removal of the phosphine ligand by small amounts of X^- in species II which incorporates a molecule of solvent when the corresponding chloride I is stable as long as one likes in concentrated solutions of X^-.

A reaction scheme based on an associative consecutive displacement mechanism (such as that in Scheme II) fails to explain either the large $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ associated with isomerization or the fact that the rate of isomerization is almost insensitive to steric crowding produced by the ligand R.

In conclusion we wish to point out that there can be a variety of mechanisms for isomerization of square-planar complexes, and it is dangerous to extrapolate from one system to another when conditions or species are changed and, at this stage at least, each system needs to be investigated by itself before its mechanism can be assumed with confidence.

References and Notes

(1) (s) G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc. A*, 1877 (1971); (b) R. Romeo, D. Minniti, and M. Tozzi, *Inorg. Chim. Acta*, **14**, L 15 (1975); (c) R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, **15**, 1134 (1976).
(2) For a review see R. Romeo, P. Uguagliati, and U. Belluco, *J. Molec. Catal.*, **1**, 325 (1976).
(3) W. J. Louw, *Inorg. Chem.*, **16**, 2147 (1977).
(4) (a) V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc. Dalton Trans.*, 1857 (1972); (b) V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc., Dalton Trans.*, 927 (1974).
(5) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw *J. Chem. Soc. A*, 2207 (1961).

Istituto di Chimica Fisica
Universitá di Messina
98100 Messina, Italy

Raffaello Romeo

Received December 6, 1977

Origin of the Word "Pnictide"

Sir:

Because there is far from universal agreement regarding whether the transition elements and the posttransition "representative" elements are to be designated subgroups "A" and "B" or the reverse in the periodic table, it is useful to have other names for them in order to prevent misunderstanding. For example, for the representative elements and ions of group 7 (F, Cl, Br, I, At), the terms halogens, halogenides, and halides are or have been used, while the corresponding terms chalcogens, chalcogenides, and chalconides are employed for the representative elements and ions of group 6 (S, Se, Te, Po, and sometimes O).

For the posttransition elements and ions of group 5 (N, P, As, Sb, Bi), the relatively new terms pnigogens (or pnicogens) and pnictides are being employed. The origin of these is, to say the least, obscure except perhaps to their coiner, but there appears to be a widespread belief that they derive from an acronym comprising the first letters of *p*hosphorus and *n*itrogen and possibly the last two letters of arsen*ic*.

It is much more probable, however, that they are derived from "pnigo", the Greek word for suffocate. Since nitrogen, which heads the subgroup, is called "stickstoff" (literally "suffocating stuff") in German, it seems extremely likely that someone chose the corresponding Greek root to coin a new name for the subgroup.

Chemistry Division
New Jersey Institute of Technology
Newark, New Jersey 07102

Lawrence Suchow

Received March 20, 1978

Large Closo Boron Hydrides

Sir:

Closo boron hydrides and metallocarboranes are among the simplest metal cluster systems.[1] Polyhedra with up to 14 vertices have been observed for metallocarboranes.[2] Recently,[3] a broad outline has been presented for future theoretical studies on closo boron hydrides with 13 to 24 boron atoms. In this note, we report some results of an extensive theoretical study of these molecules; some surprising findings are the following: (i) the discovery that some structures can have the full polyhedral symmetry only if they are neutral, i.e., contain only $2n$ framework electrons, where n is the number of vertices; (ii) the finding that there is no significant difference between the average stabilities of even and odd numbered polyhedra; (iii) the likelihood that 22 vertices represents an upper limit for truly stable structures.

All of the computations were carried out using the PRDDO (partial retention of diatomic differential overlap) approximation.[4] The standard bond lengths given previously[3] were employed. In addition, a new systematic approach to orient the hydrogens was developed, invariably providing lower calculated energies. The absolute value of the energy per BH unit, denoted $\bar{E}$, was used to compare relative stabilities. A plot of $\bar{E}$ vs. n for the most stable doubly negative structure(s) for each n ($24 \geq n \geq 9$) is given in Figure 1.

Three cases were discovered where, if the structure was treated as a doubly negative ion with $(2n + 2)$ framework electrons, it underwent Jahn–Teller distortions; in these cases the full molecular symmetry could be restored by considering the structure to be a neutral one, with only $2n$ framework electrons. In Table I we list the pertinent information on these neutral structures. A series of large, neutral closo metallocarboranes can be constructed conceptually from the neutral boron hydrides by the replacement of BH units at vertices of high connectivity by other structural moieties each of which contributes two electrons to the framework bonding. Among these, $(Co(\pi\text{-}C_5H_5))_4B_{12}H_{12}$ and $(Fe(CO)_3)_4B_{12}H_{12}$ may be considered as strong candidates for synthesis. These two examples have T_d symmetry (Figure 2), like the hypothetical parent neutral closo boron hydride structure.

Table I. Large Neutral Closo Boron Hydrides (B_nH_n, $n \geqslant 13$)

n	symmetry	label[a]	$\bar{E}$, au
16	T_d	IV	25.244
19	C_{3v}	VIIa	25.243
22	T_d	Xa	25.249

[a] The labels are those given in ref 3.

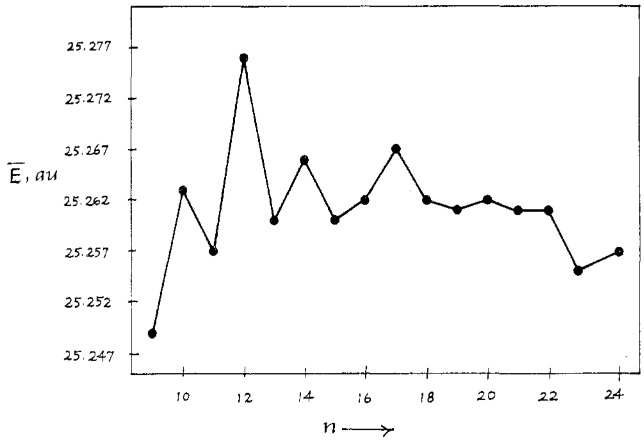

Figure 1. $\bar{E}$ (|energy| per BH unit), as a function of n for the preferred $B_nH_n^{2-}$ structures. Notation (n; n_7, n_6, n_5; point group; label in ref 3 where applicable) where n_7, n_6, and n_5 are the numbers of 7-, 6-, and 5-coordinate borons, including a terminal B–H bond for each: (9; 0, 6, 3; D_{3h}); (10; 0, 8, 2; D_{4d}); (11; 1, 8, 2; C_{2v}); (12; 0, 12, 0; I_h); (13; 2, 10, 1; C_{2v}; I); (14; 2, 12, 0; D_{6d}; IIa); (15; 3, 12, 0; D_{3h}; III); (16; 4, 12, 0; D_2); (17; 5, 12, 0; D_{5h}; Vb); (18; 6, 12, 0; D_{3d}; VIc); (19; 7, 12, 0; C_s; VIIc); (20; 8, 12, 0; D_{3h}; VIIIb); (21; 9, 12, 0; D_3; IXa); (22; 10, 12, 0; D_{5d}); (23; 11, 12, 0; D_3; XIa) and (23; 11, 12, 0; C_{2v}; XIb); (24; 12, 12, 0; T; XIIa).

Another observation (see Figure 1) is that there is no significant difference in the overall stabilities of the even and odd n large closo doubly negative structures, in contrast to the cases of n = 9–12 where $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are remarkably more stable than $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$. In particular, it can be seen that the two highest peaks in $\bar{E}$ are at n = 17 and n = 14, respectively.

Finally, it seems probable that no closo boron hydride structures with great stability will be found for $n > 22$. Even though many structures were examined with n = 23 and n = 24, none was found to be competitive with those for $n \leq 22$.

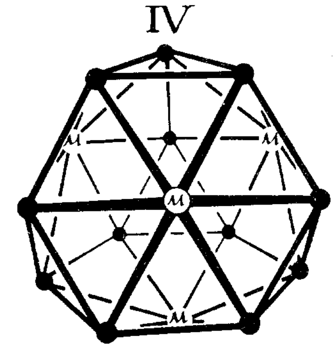

Figure 2. The 16-vertex structure of T_d symmetry. The four vertices of highest coordination number are suitable positions for a liganded transition metal.

Acknowledgment. We wish to thank the National Science Foundation for support of this research.

References and Notes

(1) R. L. Middaugh, "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975, Chapter 8, and the references cited therein.
(2) M. F. Hawthorne, *J. Organomet. Chem.*, **100**, 97 (1975).
(3) L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, **16**, 2989 (1977).
(4) (a) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58**, 1569 (1973); (b) T. A. Halgren and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 652 (1972).

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Jozef Bicerano
Dennis S. Marynick
William N. Lipscomb*

Received March 24, 1978