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(6) Tetrametallic Nickel-Boron Clusters, $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$
and $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$. Synthesis of Metalloboron Cluster
Systems by Transition Metal Aggregation on a
Small Borane Framework

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Abstract. The reaction of $\text{Na}^+\text{B}_5\text{H}_8^-$ with nickelocene and sodium amalgam in tetrahydrofuran at ambient temperature yielded the title compounds, which were isolated as crystalline solids and characterized from their ^{11}B and ^1H FT NMR and mass spectra and an X-ray structure determination of the Ni_4B_4 cluster. Although the number of skeletal valence electrons in each system is consistent with a nido structure, $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ has a closo-dodecahedral structure with rigorous D_{2d} symmetry, with all nickel atoms occupying low-coordinate vertices; this geometry contrasts with that of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$, which is also closo-dodecahedral but has the metal atoms in high-coordinate vertices. The two nickel species and the previously reported $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ are the only known examples of tetrametallic boron cage compounds, and they extend the class of metalloboron "hybrid" cluster systems which link the borane and metal cluster families. These results, together with earlier preparations of other metal-metal bonded metalloborane cages from B_5H_8^- and other boron substrates, suggest that stepwise metal attachment to a borane framework is a general phenomenon which can be utilized as a synthetic route to polymetallic cluster systems.

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Sir:

The reaction¹ of $B_5H_8^-$ ion with $CoCl_2$ and $C_5H_5^-$ in cold tetrahydrofuran (THF) generates, among other products, a series of polyhedral cobalt-boron clusters having a high metal content, e.g., $(\eta^5-C_5H_5)_2Co_2B_4H_6$, $(\eta^5-C_5H_5)_3Co_3B_3H_5$, $(\eta^5-C_5H_5)_3Co_3B_4H_4$, and $(\eta^5-C_5H_5)_4Co_4B_4H_4$, all of which have been crystallographically characterized.² The major cobaltaborane product of the reaction is the square-pyramidal complex $2-(\eta^5-C_5H_5)CoB_4H_8$, a B_5H_9 analogue; further addition of cobalt to the bridge-deprotonated anion of that species, $(\eta^5-C_5H_5)CoB_4H_7^-$, produces the same metal-rich clusters.³

The formation of these metalloboron cages can be envisioned as a stepwise aggregation of cyclopentadienylcobalt units onto a borane substrate, which thereby serves as a nucleation center. Moreover, since in each of the polyhedral cobalt-boron clusters the metal atoms show a distinct propensity to adopt adjacent vertices in the cage framework,² it appears that the presence of one or more cobalt centers in the cage promotes the further addition of cobalt.⁴ That this phenomenon is not limited to cobalt is suggested by the preparation from CB_5H_9 of a trimetallic $(\eta^5-C_5H_5)_3Ni_3CB_5H_6$ complex containing two Ni-Ni interactions,⁵ and the synthesis of a $(\eta^5-C_5H_5)_2Ni_2B_{10}H_{10}$ complex which is proposed to have adjacent metal atoms, from the $B_{10}H_{10}^{2-}$ ion.⁶ Moreover, in the closely related metallocarborane family there are numerous examples of di- and trimetallic species in which the metals kinetically adopt vicinal locations in the polyhedron (although in some cases they migrate at elevated temperature to non-vicinal positions).⁷

In this Communication we report the extension of this pattern with the synthesis of two tetranickel species which are the second and third examples [after $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4^{1b}$] of metalloboron polyhedra containing four metal atoms, and are new representatives of "hybrid" cages¹ linking the borane and metal cluster families. The treatment of 22 mmol of $\text{Na}^+\text{B}_5\text{H}_8^-$ (prepared from B_5H_9 and NaH) with 34 mmol of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ and sodium amalgam containing 36 mmol of Na in THF at -30° with subsequent stirring at 0° and finally at room temperature, gave a dark green solution. Removal of solvent in vacuo, extraction with hexane followed by CH_2Cl_2 , and separation by preparative-scale liquid chromatography on silica, afforded two major components as crystalline, air-stable solids: brown $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ (I) [0.817 g (18% yield based on $(\text{C}_5\text{H}_5)_2\text{Ni}$ consumed), $R_f = 0.60$] and green $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$ (II) [0.465 g (10%), $R_f = 0.49$]. The mass spectra of I and II exhibited strong parent groupings with intensity patterns conforming to the compositions indicated above. Exact mass determinations: for I, calc. for $^{60}\text{Ni}_4^{12}\text{C}_{20}^{11}\text{B}_4^1\text{H}_{24}^+$, 547.9578; found, 547.9576 ; for II, calc. for $^{60}\text{Ni}_4^{12}\text{C}_{20}^{11}\text{B}_5^1\text{H}_{25}^+$, 559.9750; found, 559.9743.

The 100-MHz ^1H FTNMR spectrum of I in CDCl_3 exhibited a single C_5H_5 resonance at δ 5.34 ppm¹⁰ relative to $(\text{CH}_3)_4\text{Si}$, and an H-B singlet (^{11}B -decoupled) at δ 8.22 ; the ^1H spectrum of II contained C_5H_5 singlets at δ 5.45, 5.35, and 5.29 with relative areas of 5:10:5, and H-B resonances (^{11}B -decoupled) at δ 8.80, 7.25, and 4.70 with relative areas of 2:1:2. The 32-MHz ^{11}B FTNMR spectrum of I exhibited one doublet at δ 56.2 ppm¹⁰ relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ ($J_{\text{BH}} = 156$ Hz), which collapsed to a singlet on ^1H decoupling. The ^{11}B spectrum of

II exhibited doublets at δ 64.7 ($J = 156$, area 2), 55.0 ($J = 157$, area 1), and 29.4 ($J = 117$, area 2), all of which collapsed to singlets on ^1H -decoupling.

Since I and II contain 20 and 22 skeletal valence electrons (based on a donation¹¹ of 3 from each $(\text{C}_5\text{H}_5)\text{Ni}$ and 2 from each BH unit), both species are $(2n+4)$ -electron systems (n = the number of vertices) and thus were expected to adopt nido¹² structures. However, X-ray diffraction data¹⁴ on I has established the closo dodecahedral (D_{2d}) geometry shown in Figure 1a. This structure is surprising not only in that it is closo rather than nido, but also in the fact that all four metal atoms occupy low-coordinate vertices with unusually short¹⁵ equivalent Ni-Ni distances of 2.354(1) Å. Curiously, the recently reported^{1b,c} cluster $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ (which has four fewer electrons than I) also adopts a closo dodecahedral shape^{1c,2b} but with all metal atoms in high-coordinate vertices. It is remarkable that the 8-vertex species $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$, $\text{B}_8\text{H}_8^{2-}$, $\text{C}_2\text{B}_6\text{H}_8$, and $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$, which are assigned, respectively, 20, 18, 18, and 16 skeletal valence electrons, all exhibit the same (closo) polyhedral geometry. The structure of $(\text{CH}_3)_4\text{C}_4\text{B}_4\text{H}_4$,¹⁸ a 20-electron analogue of I, has not been established although several nido geometries have been suggested.¹⁸

Clearly, 8-vertex clusters present a special case in which the cage structure is markedly affected by factors above and beyond framework electron population per se.¹⁹ Indeed, a recent MO study²¹ indicates that $\text{B}_8\text{H}_8^{2-}$ is uncommon among the polyhedral borane anions in having very small energy differences between alternative geometries. Of significance in the present case may be the short nickel-nickel bond lengths

in I, which suggest abnormally high bond orders for these interactions (there do not appear to be any particular steric constraints in this system that would produce such an effect).

The structure of II has not been established, but the geometry shown in Figure 1b is proposed on the basis of ^{11}B and ^1H NMR data, and on the assumption that there is a straightforward structural relationship between I and II (it is likely that I forms by net loss of a BH unit from II). Thus, a direct $\text{II} \rightarrow \text{I}$ conversion can be effected by removing B(6)-H from II and linking B(9) to B(3) and Ni(7). In view of the fact that the 8-vertex species I is *closo*, in violation of the structural electron count rules,¹¹ it is possible that a similar anomaly exists in II and that a *closo* structure will be found here also. However, as noted above, I and other 8-vertex clusters are regarded as an exceptional group; moreover, the trinickel metallocarborane⁵ $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{CB}_5\text{H}_6$, an isoelectronic analogue of II, has an established *nido* geometry similar to that proposed here for II. Hence we expect II to adopt a *nido* structure as shown, in conformity with the presence of 22 skeletal electrons.¹¹

Since cobalt and nickel can be incorporated into B_5H_8^- to give polymetallic clusters, extension to other metals and to other borane substrates seems likely; however, because the nature of the products is largely controlled by kinetic factors, the choice of reagent is crucial. Thus, the treatment of B_5H_8^- with FeCl_2 and C_5H_5^- produces monoferraboranes²² such as $2-(\eta^5\text{-C}_5\text{H}_5)\text{FeB}_5\text{H}_{10}$ rather than metal-rich species. Investigations in this area are continuing.

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References and Notes

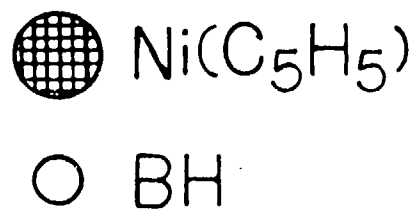
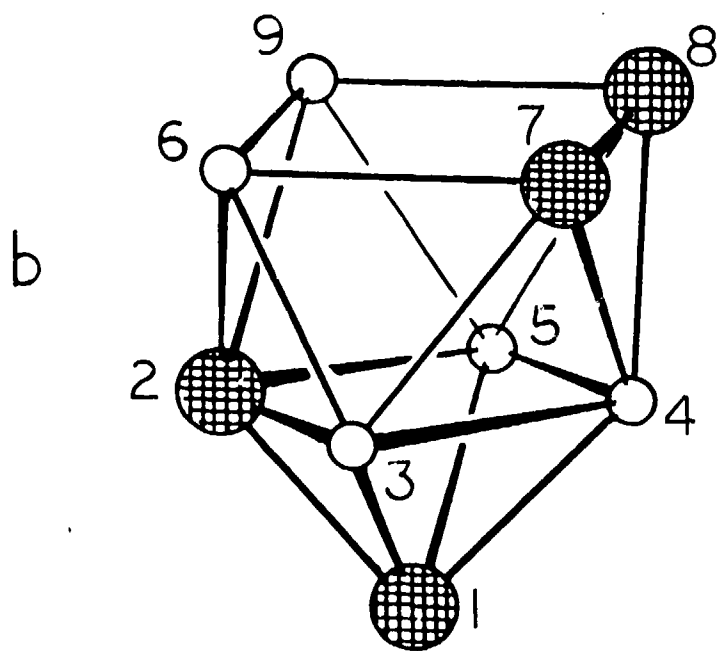
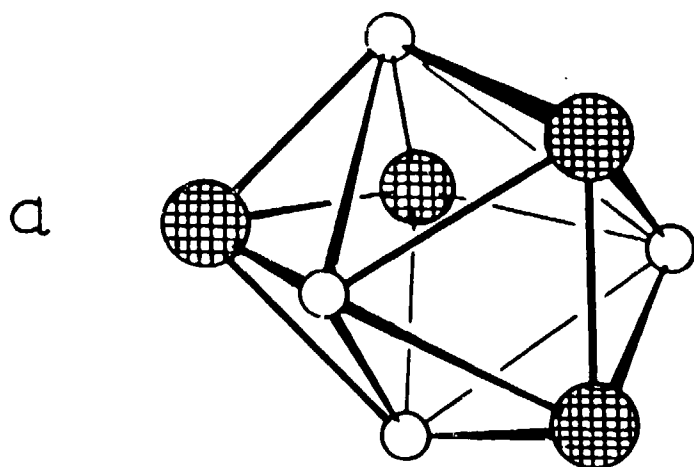
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 nickel clusters, although Ni-Ni bond lengths in the range 2.34-
 2.38 Å have been found in small nickel carbonyl clusters.¹⁷

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Figure Caption

Figure 1. (a) Structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ (I). (b) Proposed structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$ (II). The molecule is bisected by a mirror plane through Ni(1), Ni(2), and B(4).



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