

References and Notes

- (a) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976); (b) G. C. Demitras and E. L. Muetterties, *ibid.*, **99**, 2796 (1977); (c) E. Band, W. R. Pretzer, M. G. Thomas, and E. L. Muetterties, *ibid.*, **99**, 7380 (1977); (d) M. A. Andrews and H. D. Kaesz, *ibid.*, **99**, 6763 (1977); (e) W. R. Roper and K. G. Town, *J. Chem. Soc., Chem. Commun.*, 781 (1977); (f) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).
- I is formed by adding phenyl isocyanide dropwise to a concentrated solution of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ in pentane until the solution turns yellow (1–2 min). Vigorous stirring induces precipitation (< 10 min) of I. With cooling (-20°C) the yield becomes essentially quantitative.
- (a) J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, **97**, 4145 (1975); (b) A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, **114**, 313 (1976).
- M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
- M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 2397 (1977).
- Satisfactory elemental analysis have been obtained. Variable-temperature ^1H NMR spectra indicate that I exists as mixture of two isomers and is also fluxional (i.e., bridging and terminal hydride ligands are rapidly interconverting at room temperature).
- The reaction is characterized by a purple coloration which develops and disappears within the first 10–15 min, and proceeds to completion over a period of ~ 2 h. At completion, II is formed in up to 70% yield. The isolation and characterization of intermediates in the transformation $\text{I} \rightarrow \text{II}$ is now being carried out. II was isolated by chromatography over alumina/6% H_2O and crystallized from hexane solvent: IR ν (CO) 2090 (m), 2065 (s), 2035 (s), 2010 (s), 2000 (s), 1990 (s), 1970 (m) cm^{-1} .
- II crystallizes in the monoclinic space group $P2_1/n$; $a = 8.518$ (3) Å, $b = 8.095$ (2) Å, $c = 30.141$ (4) Å, $\beta = 93.85$ (2) $^\circ$. Diffraction data were collected on a CAD-4 automatic diffractometer; 2468 reflections ($F^2 > 3.0\sigma(F^2)$) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. All programs used were those of the Enraf-Nonius structure determination program library, and all calculations were done on a PDP 11/45 computer. Final residuals were $R = 0.034$ and $R_w = 0.040$.
- Os(1)–Os(2) = 2.956 (1), Os(1)–Os(3) = 2.797 (1), Os(2)–Os(3) = 2.740 (1), Os(1)–C(10) = 2.03 (1), Os(2)–N = 2.12 (1), Os(3)–C(10) = 2.27 (1), Os(3)–N = 2.22 (1), C(10)–N = 1.415 (11), N–C(11) = 1.478 (13) Å.
- Kaesz^{1d} has recently discussed a structurally similar compound which was observed as an intermediate in the cluster catalyzed reduction of organonitriles. An analogous structure has been proposed for the compound, $\text{HOs}_3(\text{CO})_9(\text{CHNCH}_3)_3$, which was prepared by the reaction of $\text{Os}_3(\text{CO})_{12}$ with trimethylamine.¹¹
- C. C. Yin and A. J. Deeming, *J. Organomet. Chem.*, **133**, 123 (1977).
- E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).
- There have been previous reports of isocyanide insertions into metal-hydride bonds.¹⁴
- (a) D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 458 (1972); (b) D. F. Christian, H. C. Clark, and R. F. Stepaniak, *J. Organomet. Chem.*, **112**, 209 (1976); (c) D. F. Christian and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 2556 (1975); (d) D. F. Christian and W. R. Roper, *J. Organomet. Chem.*, **80**, C35 (1974).
- E. L. Muetterties, *Science*, **196**, 839 (1977), and references therein.

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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

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., $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_4\text{H}_6$, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_3\text{H}_5$, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4$, and $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$, all of which have been crystallographically characterized.² The major cobaltaborane product of the reaction is the square-pyramidal complex 2- $(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_8$, a B_5H_9 analogue; further addition of cobalt to the bridge-deprotonated anion of that species, $(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_7^-$, 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.

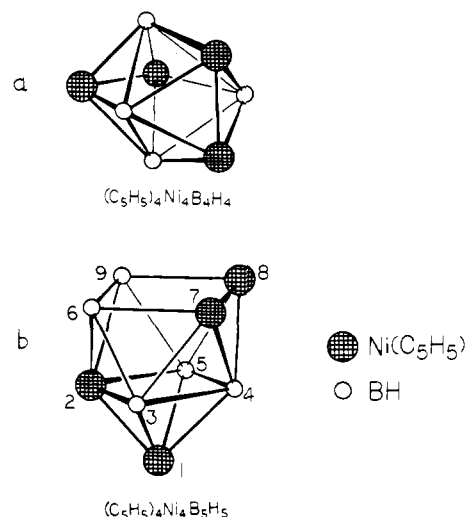


Figure 1. (a) Structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ (I). (b) Proposed structure of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_5\text{H}_5$ (II). The molecule is bisected by a mirror plane through Ni(1), Ni(2), and B(4).

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 $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{CB}_5\text{H}_6$ complex containing two Ni–Ni interactions,⁵ and the synthesis of a $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ complex which is proposed to have adjacent metal atoms, from the $\text{B}_{10}\text{H}_{10}^{2-}$ 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 nonvicinal positions).⁷

In this communication we report a major 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,c}) 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°C , with subsequent stirring at 0°C 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, calculated for $^{60}\text{Ni}_4^{12}\text{C}_{20}^{11}\text{B}_4^1\text{H}_{24}^+$ 547.9578, found 547.9576; for II, calculated 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 FT NMR 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 FT NMR 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 ($J = 156$ Hz, area 2),

55.0 ($J = 157$ Hz, area 1), and 29.4 ($J = 117$ Hz, area 2), all of which collapsed to singlets on ^1H decoupling.

Since I and II formally 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 have 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 $2\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{FeB}_5\text{H}_{10}$ rather than metal-rich species. Investigations in this area are continuing.

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References and Notes

- (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) V. R. Miller and R. N. Grimes, *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).
- (a) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977); (b) J. R. Pipal and R. N. Grimes, submitted for publication.
- R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978).
- The condensation of Co atoms with B_5H_9 and cyclopentadiene at -196°C yields the same cobalt–boron clusters as were originally reported in

ref 1a–c, as well as a new one, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_5\text{H}_5$, of uncertain structure: L. W. Hall, G. J. Zimmerman, and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, 45 (1977).

- (5) C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976).
- (6) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 455 (1975).
- (7) The adjacent-metal effect is most evident in the smaller polyhedral species⁸ (perhaps in part owing to the more limited geometric options), but examples can also be found among the icosahedral or supraicosahedral metallocarboranes.⁹
- (8) (a) G. K. Barker, M. Green, J. L. Spencer, F. G. A. Stone, B. F. Taylor, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 804 (1975); (b) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974); (c) V. R. Miller and R. N. Grimes, *ibid.*, **97**, 4213 (1975); (d) C. G. Salentine and M. F. Hawthorne, *ibid.*, **97**, 6382 (1975); (e) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *ibid.*, **97**, 296 (1975); (f) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *ibid.*, **98**, 4818 (1976); (g) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976); (h) W. M. Maxwell, K.-S. Wong, and R. N. Grimes, *ibid.*, **16**, 3094 (1977).
- (9) (a) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974); (b) W. J. Evans and M. F. Hawthorne, *ibid.*, **13**, 869 (1974); (c) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *ibid.*, **13**, 1397 (1974).
- (10) Positive values indicate shifts to lower field (less shielding).
- (11) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976); (c) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).
- (12) Cages based on closo (triangulated) polyhedra with one missing vertex are described as nido, while those with two vacant vertices are labeled archno.^{11,13}
- (13) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).
- (14) J. R. Pipal and R. N. Grimes, to be published.
- (15) Metal–metal bond distances in other metallocarboranes and metallocarboranes^{16a} exceed 2.40 Å, except for that in icosahedral $(\text{C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_8\text{H}_{10}$ (2.387 (2) Å).^{16b} The same is true of most nickel clusters, although Ni–Ni bond lengths in the range of 2.34–2.38 Å have been found in small nickel carbonyl clusters.¹⁷
- (16) (a) See ref 2a and 5, and references therein. (b) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1397 (1974).
- (17) G. Longoni, P. Chini, L. D. Lower, and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 5034 (1975), and references therein.
- (18) T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977).
- (19) Eight-vertex metallic and organometallic clusters also exhibit a variety of polyhedral shapes including cubic, distorted cubic, and chair, e.g., $(\text{CO})_8\text{Ni}_8[\mu_4\text{-P}(\text{C}_6\text{H}_5)]_8$,^{20a} $(\eta^5\text{-C}_5\text{H}_5)_4\text{Fe}_4\text{S}_4$,^{20b} and $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ag}_4$.^{20c}
- (20) (a) L. D. Lower and L. F. Dahl, *J. Am. Chem. Soc.*, **98**, 5046 (1976); (b) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *ibid.*, **99**, 402 (1977); (c) B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2474 (1976).
- (21) E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975).
- (22) R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 8087 (1977).

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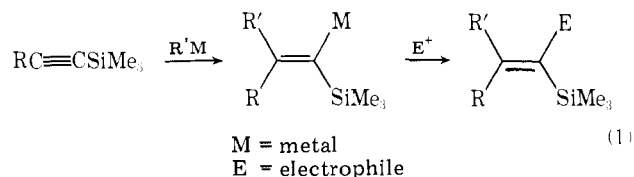
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Nickel-Catalyzed Addition of Grignard Reagents to Silylacetylenes. Synthesis of Tetrasubstituted Alkenes

Sir:

Vinylsilanes have recently been shown to be versatile synthetic intermediates¹ which react with a wide variety of electrophiles, undergoing desilylation with retention of stereochemistry.^{1,2} We are interested in developing reactions of organometallic reagents with silylacetylenes to provide new stereospecific routes to di- and trisubstituted vinylsilanes (eq 1). Although the hydroboration³ and hydroalumination⁴ of



silylacetylenes are known, there are no carbometalation reactions of silylacetylenes of general applicability. The cis addition of organocopper species $(\text{RCu}\cdot\text{MgX}_2)$ to terminal