Pure Appl. Chem., Vol. 75, No. 9, pp. 1219–1229, 2003.

Recent advances in the chemistry of carboranes and metallacarboranes*

Narayan S. Hosmane

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115-2862, USA

Abstract: An overview of the syntheses, structures, and reactivity of the compounds formed by the incorporation of a number of *d*- and *f*-block metals into C_2B_4- and C_2B_9-carborane cages have been presented. In addition, the development of a safe, bench-scale preparation of the toxic and commercially unavailable polyhedral borane synthon, namely pentaborane(9), has also been described. Thus, this report discusses the latest developments leading to a systematic synthetic approach to a number of carborane precursors and the subsequent reaction chemistry in the formation of a number of "carbons-apart" metallacarboranes.

INTRODUCTION

There has been extensive research reported on the chemical and structural properties of the metallacarboranes in the pentagonal bipyramidal (MC_2B_4) and the icosahedral (MC_2B_9) cage systems [1]. These complexes are generally synthesized by the reaction of the mono- or dianions of the *nido*-C_2B_4 or C_2B_9 carboranes with suitable metal reagents. Much of the emphasis for these studies comes from the fact that the two *nido*-carboranes have 6 π-electrons delocalized on a C_2B_3 open pentagonal face that are very similar to the primary metal-bonding orbitals of the cyclopentadienide ligand, $[C_5H_5]^-$. Our research in this area has involved synthetic, structural, reactivity, and theoretical studies on the full- and half-sandwich metallacarboranes derived from the interactions of [*nido*-2-($SiMe_3$)-*n*-(R)-2,*n*-$C_2B_4H_4]^{2-}$ [*n* = 3, 4; R = $SiMe_3$, *n*-Bu, *t*-Bu, Me, H] with main group [2], *d*-group, [3] and *f*-group metals [4]. One of the greatest factors in promoting the study of the small-cage C_2B_4 carborane systems was the almost limitless supply of the pentaborane(9) (B_5H_9), obtained from an extensive U.S. government surplus, which can then be reacted with a suitable alkyne to form the carborane. At present, that source is no longer available, nor is there a commercial source to take its place [5]. In order for research to continue in this area, a new, convenient, and safe method of producing the pentaborane(9) must be developed. Ideally, what is desired is a one-pot method of generating pentaborane(9) from a readily available starting material, such as $NaBH_4$, which could then further react with the appropriate alkyne to generate, in situ, the corresponding small-cage carborane. Therefore, a significant effort was made to investigate an alternative, safe, and convenient method of producing pentaborane(9) starting from readily available boric acid. Although the production of carborane from $NaBH_4$, without the isolation of pentaborane, was not yet fully accomplished, the pentaborane synthesis by oxidative cage fusion of $[B_3H_8]^-$ anion was exemplified as the first step toward reaching the desired synthetic goal. In search for alternative carborane ligands, we embarked on the construction of $C_{(cage)}$-appended alkyl- and silyl-amido- and alkyloxo-derivatives of the larger C_2B_9-cage systems and to investigate their reactivity toward group 4 and group 14 metals to prepare metallacarboranes with new geometries as potential cat-

*Lecture presented at the XIth International Meeting on Boron Chemistry (IMEBORON XI), Moscow, Russia, 28 July–2 August 2002. Other presentations are published in this issue, pp. 1157–1355.

alysts or their precursors. In addition, a new methodology for the reductive cage opening of the *closo*-carboranes with in situ metalation to form the corresponding stable half- or full-sandwich metallacarborane species were explored.

Synthesis of ^{10}B-enriched pentaborane(9) from boric acid and its conversion to *nido*-$^{10}B_{10}H_{14}$ and *anti*-$^{10}B_{18}H_{22}$

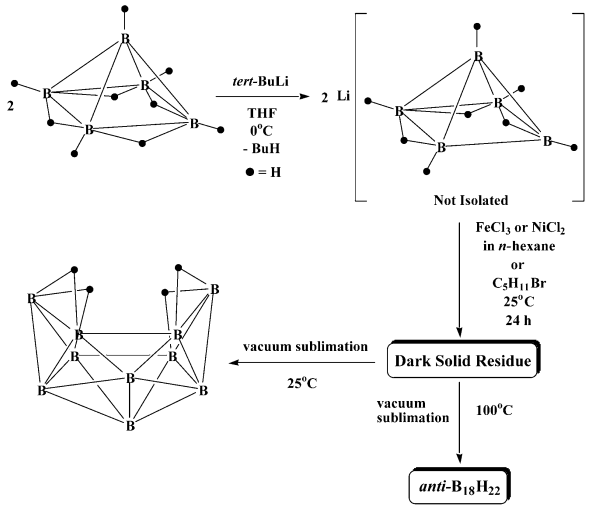
Pentaborane(9) has already been proven to be an important synthon for a number of higher polyhedral borane cages, including $[B_9H_{14}]^-$ [6], $[B_{11}H_{14}]^-$ [7], $[B_{12}H_{12}]^{2-}$, and other cage-expanded borane anions, [8] and the neutral decaborane, $B_{10}H_{14}$ [9]. The corresponding ^{10}B-enriched species are the precursors for a number of potential boron drugs for use in the clinical trials using boron neutron capture therapy (BNCT). Since there is no commercial source available for any of these species with the exception of the most expensive $^{10}B_{10}H_{14}$ [10], a convenient synthesis for hitherto unisolated ^{10}B-enriched pentaborane(9) has an obvious appeal. It is this incentive that led us to explore alternative routes to ^{10}B-enriched polyhedral boranes starting from readily available boric acid, $H_3{}^{10}BO_3$. Specifically, the ^{10}B-enriched boric acid, $H_3{}^{10}BO_3$, was converted to the corresponding sodium borohydride, $Na^{10}BH_4$, in essentially quantitative yields, by using slightly modified literature methods that involve the formation of butyl borate, $(n\text{-OBu})_3{}^{10}B$, first and then reacting it with NaH in mineral oil at 250 °*C* [11,12]. The subsequent oxidation reaction of $Na^{10}BH_4$ with I_2 in diglyme, followed by the addition of dioxane during the purification step, gave the dioxane-complexed sodium salt of octahydrotriborate (–1), $Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$, in almost quantitative yields (see eq. 1) [13].

$$3Na^{10}BH_4 + I_2 \text{ (in diglyme/dioxane)} \rightarrow 2H_2 + 2NaI + Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2) \quad (1)$$

Treatment of $Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$ with $NiCl_2$ in anhydrous benzene or heavy mineral oil at 110 °C (see eq. 2) gave the corresponding $^{10}B_5H_9$ as the first isolated ^{10}B-enriched pentaborane(9) in a laboratory environment [14]. Although there have been a number of other methods for the preparation of natural B_5H_9 [15,16], the reaction written in eq. 2 is by far the most convenient and straightforward method of choice to date.

$$2Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2) + NiCl_2 \xrightarrow[\substack{-2NaCl/-Ni^0\\ -2C_4H_8O_2}]{\substack{\text{Benzene or}\\ \text{heavy mineral oil}\\ 110\ ^\circ\text{C/12 h}}} {}^{10}B_5H_9 + 2H_2 + C_4H_8O_2\cdot {}^{10}BH_3 \quad (2)$$

Since the ^{10}B-enriched pentaborane is the only borane product of high volatility, its safe production, easy isolation, and storage in heavy mineral oil make this method most attractive to not only those who work with small-cage (C_2B_4) carboranes and metallacarboranes, but also to the laboratories that did not have the access to this material previously. Nonetheless, ^{10}B-enriched decaborane, $^{10}B_{10}H_{14}$, is the key chemical in preparing almost all of the $C_{(cage)}$-substituted bio-boron molecules that are being investigated as boron drugs for BNCT clinical trials in the United States and the world [17]. This incentive led us to investigate an alternative route for the synthesis of $^{10}B_{10}H_{14}$, from $^{10}B_5H_9$ that can be prepared as described above. Although the synthetic methodology is identical to that used for anti-$^{10}B_{18}H_{22}$ except for the oxidizing agent (Scheme 1), the room-temperature, high-vacuum sublimation of the product, instead of heating it to 100 °C, produced pure $^{10}B_{10}H_{14}$ in over 50 % yield [18a]. The conversion of natural pentaborane(9) to decaborane(14) has been previously demonstrated by Brewer and Grimes using the iron(II)- and iron(III) chloride-mediated cage fusion reactions [18b]. Thus, this work constitutes the first systematic synthetic approach to pentaborane(9) and decaborane(14) of both natural and ^{10}B-enriched analogs and to their cage-expanded neutral and anionic borane species [14,18].

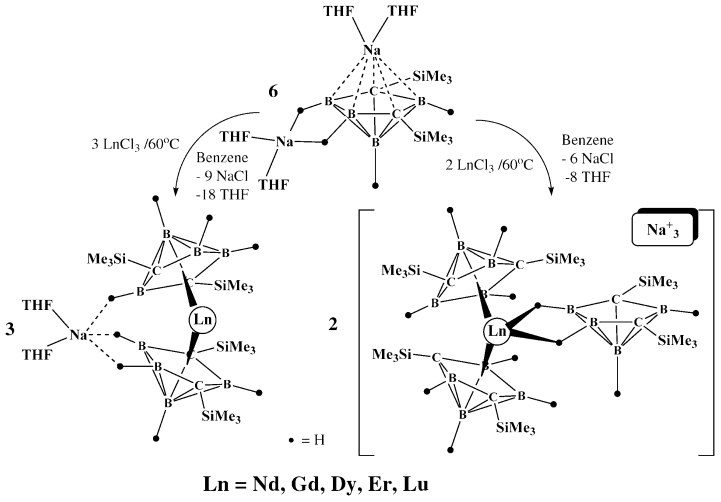


Scheme 1 Synthesis of *nido*-$^{10}B_{10}H_{14}$ and *anti*-$^{10}B_{18}H_{22}$ from $^{10}B_5H_9$.

Reductive cage-opening process with concomitant metalation of the resulting carborane ligand: A novel route to metallacarborane synthesis

The two-electron reductive cage opening of the *closo*-carboranes, in both the C_2B_{10} and C_2B_4 cage systems, have been well documented in the literature [19,20]. In all cases, the use of naphthalene, as the electron-transfer reagent, along with an alkali metal was essential for the reaction to begin and then proceed irreversibly to form the corresponding thermodynamically stable dianionic *nido*-cages in which the cage carbons are always separated by a boron atom [21].

The use of naphthalene in the traditional two-electron reductive cage-opening reactions has several disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the *nido*-carborane products can be reacted further. In addition, naphthalene also has a tendency to cocrystallize with any product or to substitute for a terminal B–H hydrogen, which often interferes with the reactivity of these dianionic ligands. The subsequent metalations of these ligands, in the conventional synthetic procedure, shown in Scheme 2, produce metallacarboranes of different geometries



Ln = Nd, Gd, Dy, Er, Lu

Scheme 2 Conventional synthetic route for lanthanacarboranes.

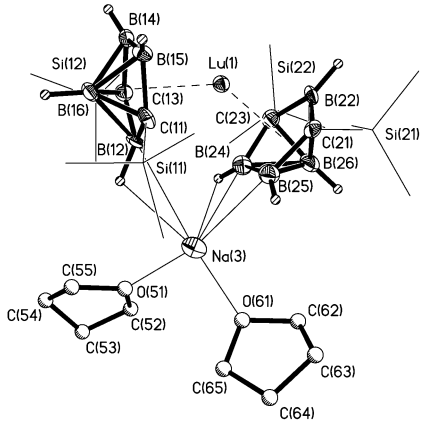


Fig. 1 Lutetiacarborane sandwich.

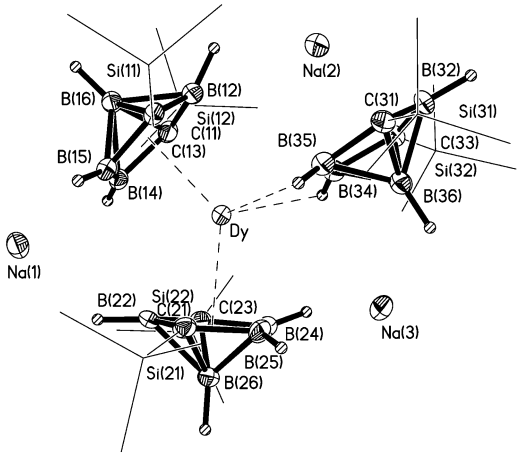
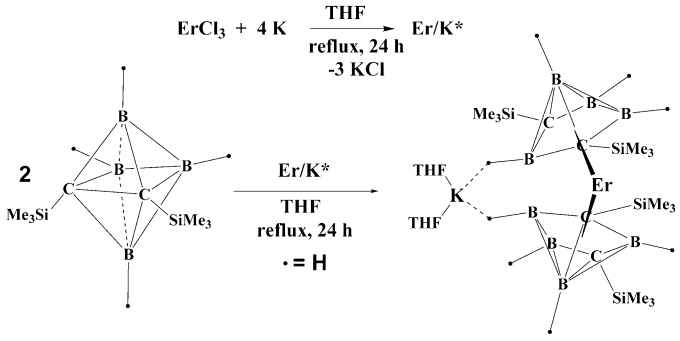


Fig. 2 Dysprosacarborane sandwich.

depending on the ratios of reactants involved [22–31]. The structures of the representive compounds are depicted in Figs. 1 and 2 [30,31].

The inability of the *closo*-carboranes to undergo reduction in the absence of naphthalene led us to question whether such carboranes could be reductively opened by the in situ generation of reactive metal atoms whose cations are good coordinators of the carborane. To explore this possibility, anhydrous $ErCl_3$ was reacted with 4 equiv of freshly cut potassium metal, under refluxing conditions in THF, to produce what we believe to be an active erbium metal alloy of the form of Er/K* (Scheme 3) [32]. The alloy was immediately treated with the *closo*-carborane, 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$, which after refluxing overnight with constant stirring, produced a light-orange crystalline solid, identified as the "carbons apart" erbacarborane sandwich, 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4)_2$, in 82 % yield (see Scheme 3) [32]. It is important to note that, under the same reaction conditions, neither the Er or K metal alone nor the one generated in situ by reacting K with $ErCl_3$ in 3:1 ratio, underwent reductive cage opening; in both cases the *closo*-carborane precursor was recovered unchanged. Although the Na/Hg alloy has been widely used in coupling reactions of many organometallic species [33], there have been no reports of its use either in the reductive cage-opening of the carboranes or in the synthesis of mercuracarborane complexes. Therefore, the reaction shown in Scheme 3 is an unprecedented ex-



Scheme 3 Reductive cage-opening with concomitant metalation of the carborane ligand.

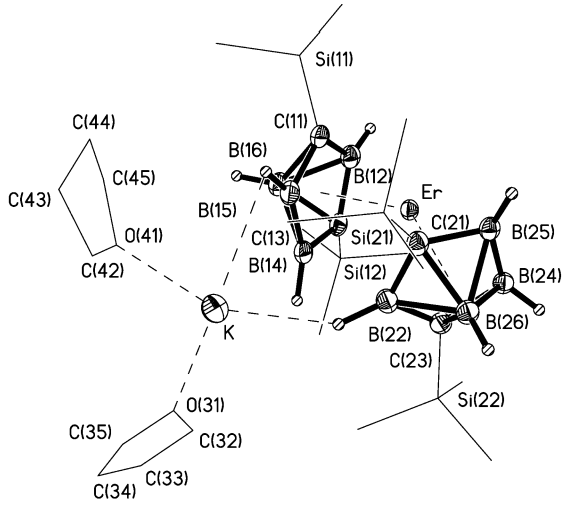
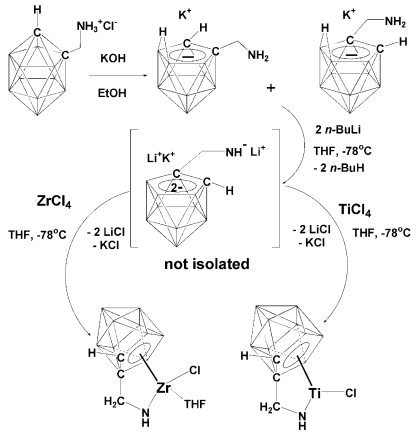


Fig. 3 Erbacarborane sandwich.

ample of a new reductive cage-opening process that should prove applicable to the *closo*-carboranes in both the icosahedral and subicosahedral cage systems, and lead to the formation of hitherto unknown metallacarborane species.

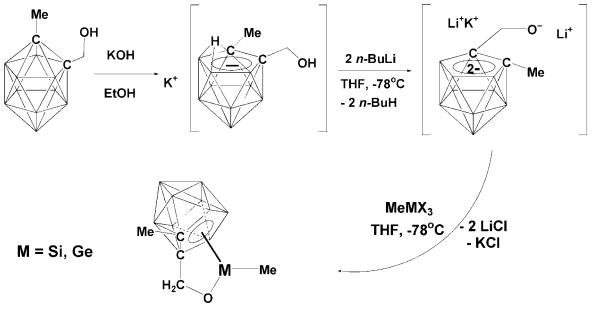
Chemistry of half-sandwich, constrained-geometry C_2B_9-metallacarboranes

The potential applications of functionalized carborane clusters in catalytic organic reactions have resulted in the reports of the syntheses and reactivities of a number of new metallacarboranes [34]. Our preliminary research in this area has shown that the trianionic ligand [*nido*-7-(CH_2NH)-7,8-$C_2B_9H_{10}]^{3-}$, prepared from the reaction of [*nido*-7-(CH_2NH_2)-7,8-$C_2B_9H_{11}]^-$ with 2 equiv of *n*-BuLi, reacts with MCl_4 (M = Ti, Zr) to give the corresponding half-sandwich metallacarboranes (Scheme 4) [35]. Nevertheless, there have been a handful of reports in which the appended moiety forms either a coordinate covalent bond or another delocalized π-bond with the metal atom *exo*-polyhedrally, and none demonstrated the additional stabilization of the metal by sigma bonding to the $C_{(cage)}$-appended moiety [34]. Therefore, our results are the first examples of half-sandwiched group 4 metallacarboranes in which the nitrogen atom of the *exo*-polyhedral $C_{(cage)}$-alkylamido unit is η^1(sigma)-bonded to the metal that is complexed with the open C_2B_3-bonding face of the carborane ligand (Scheme 4). These observations suggested the possibility of using other constrained-geometry ligands, such as the *ansa*-alky-



Scheme 4 Synthetic scheme for *ansa*-alkylamidometallacarboranes.

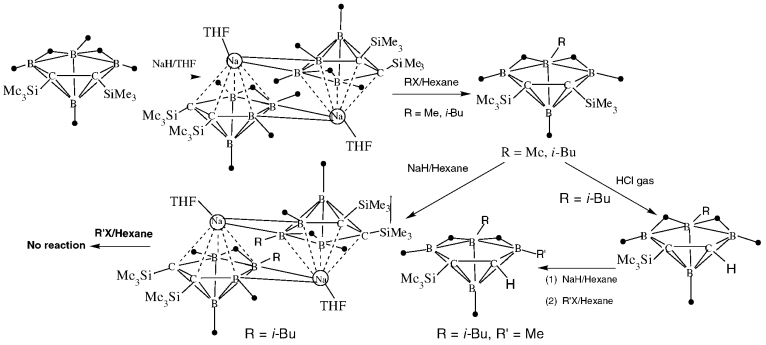
loxocarborane, to prepare a series of $C_{(cage)}$-appended half-sandwich alkyloxometallacarboranes (Scheme 5). Thus, the in situ generated trianionic ligand was further reacted with anhydrous $MeMCl_3$ (M = Si, Ge), followed by recrystallization from a toluene/heptane solution to form the corresponding half-sandwich group 14 metallacarboranes, *closo*-1-M(Me)-2-(1-$\eta^1(\sigma)$-OCH_2)-3-Me-η^5-2,3-$C_2B_9H_9$ [M = Si, Ge], in 48 and 56 % yields, respectively. The NMR spectra, IR spectra, and the microanalytical data for these species confirmed their formulations as shown in Scheme 5 [36]. The reactivities of these constrained-geometry metallacarboranes, especially of the group 4 metals, toward olefinic substrates are currently underway in our laboratories.



Scheme 5 Synthetic scheme for *ansa*-alkyloxometallacarboranes.

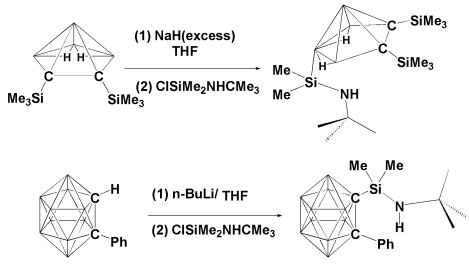
Syntheses and reactivities of $B_{(cage)}$-alkyl- and silylamido-C_2B_4-carboranes

In order to investigate the reactivities of alkylated and polyalkylated carboranes, we have initiated a study of the regiospecific alkylation of the *nido*-2,3-$(SiMe_3)_2$2,3-$C_2B_4H_6$ and an investigation of the chemical behavior of any B-alkylated products. The following specific questions were addressed: (1) Is it possible to systematically alkylate and/or polyalkylate carboranes having such bulky substituents as the $SiMe_3$ groups? (2) If so, what is the effect of the $SiMe_3$ groups in determining the distribution of products? (3) Could any alkylated product undergo standard deprotonation and oxidation reactions preparatory to the formation of metallacarboranes and the carbons apart analogs, respectively? And (4) how effective are the standard techniques of ^1H, ^{11}B, and ^{13}C NMR spectroscopy in identifying the structures of any alkylated products? Therefore, the reaction of the sodium compound of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ with the standard alkyllating agents, MeI and *i*-BuBr, was carried out to produce the corresponding neutral monoalkylated carboranes, *nido*-5-(R)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (R = Me



Scheme 6 Systematic $B_{(cage)}$-alkylation of the the *nido*-2,3-$(SiMe_3)_2$2,3-$C_2B_4H_6$.

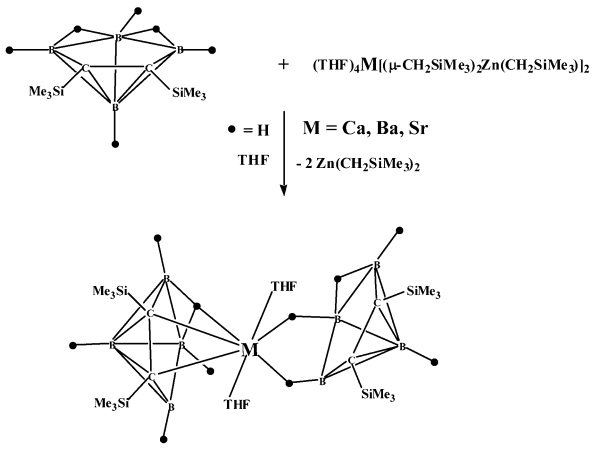
and *i*-Bu) in 75 % yields, respectively (Scheme 6) [37]. The alkylation reaction seems to be a general one, that leads exclusively to $B_{(unique)}$-alkylated products. The alkylation reactions are presumably through an intermediate in which the incoming alkyl unit is bridged between the unique boron and one of its neighboring basal borons. The intermediate then collapses with the alkyl group migrating to the terminal position of one of the two borons, changing places with its terminal hydrogen. The difference in the directing ability of the $SiMe_3$ compared to the C-alkyl groups is most likely due to the steric bulk of the $SiMe_3$ moiety. This unique directive property of the $SiMe_3$ group was profitably exploited in the synthesis of the corresponding $B_{(cage)}$-silylamido-substituted carborane derivatives. The reaction of the sodium salt of the [*nido*-2,3-$(SiMe_3)_2C_2B_4H_5]^-$ anion with (*t*-butylamido)dimethylchlorosilane, in a 1:1 ratio in THF, followed by extraction and purification, produced a new $B_{(unique)}$-substituted small-cage carborane, *nido*-2,3-$(SiMe_3)_2$-5-[$Si(Me_2)NH(Me_3C)$]-2,3-$C_2B_4H_5$ in 85 % yield (Scheme 7) [38]. In a similar procedure, the monolithium salt of [*closo*-1-Ph-1,2-$C_2B_{10}H_{10}]^-$ anion reacts with the same substituted siliane, produced a colorless sticky liquid of *closo*-1-Ph-2-[$Si(Me_2)NH(Me_3C)$]-1,2-$C_2B_{10}H_{10}$ in 92 % yield as shown in Scheme 7. The reactivity study of these species is currently in progress.



Scheme 7 Syntheses of $B_{(cage)}$- and $C_{(cage)}$-silylamido-substituted carboranes.

Novel synthetic approach to heavier group 2 metallacarboranes

The reaction of tetrakis(tetrahydrofuran)bariumbis[tris(trimethylsilylmethyl)zincate] with 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane in THF yields nearly quantitatively the bis(carborane)barium complex according to Scheme 8 [39]. Only one of the trimethylsilylmethyl groups of the zincate is active in this metalation reaction. The formed bis(trimethylsilylmethyl) zinc neither reacts with the carborane nor with the bis(carborane)barium complex. Each barium atom in the dimeric structure of the complex shows a coordination number of nine, which is depicted in Fig. 4. The Ba–O bond lengths of approximately 274 pm lie in the expected region. Furthermore, two carborane ligands are bonded via hydride bridges with Ba–H distances of approximately 290 pm, which were refined isotropically and can be interpreted as Ba–H–B three-center bonds. A third carborane ligand is coordinated



Scheme 8 Syntheses of heavier group 2 metallacarboranes.

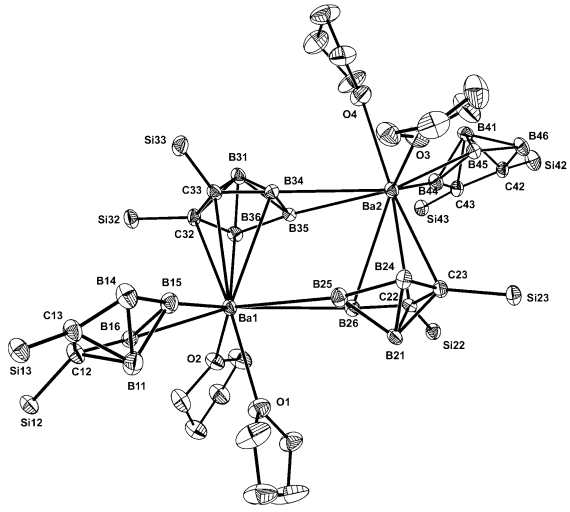


Fig. 4 Structure of a baracarborane complex.

with Ba–C distances of 316 pm and the bridging hydrogen atom [Ba1–H356 = 293(4) pm]. This situation corresponds to a four-center $BaHB_2$ bond. In the highly ionic solvated $Ba(BH_4)_2$ the boranate anions coordinate via three H atoms to the alkaline earth metal, thus forming three-center Ba–H–B bonds [40]. The Ba–C distances are similar to those of the barium bis[tris(trimethylsilylmethyl)zincates] [41] where bridging trimethylsilylmethyl moieties between barium and zinc were found. The Ba–C distances of substituted barocenes vary between 290 and 300 pm [42]. This coordination of the carborane to the barium center is quite different than that observed for the carborane complexes of magnesium and calcium [22,43–45]. In the magnesacarborane complex, the metal center bonds to the hydride substituents but not to the carbon atoms. With the doubly deprotonated carborane ligands the metal centers show shorter contacts to the borons than to the carbon atoms. In the barium complex very long Ba–B bonds are observed due to the coordination geometry about the metal center. Nevertheless, this baracarborane was the first known example of the heaviest group 2 metallacarborane. Similarly, the corresponding calca- and strontacarboranes were synthesized and structurally characterized [46].

ACKNOWLEDGMENTS

This work was supported by grants from the National Science Foundation (CHE-9988045 and CHE-0241319), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Northern Illinois University through Presidential Research Professorship. The Forschungspreis der Alexander von Humboldt-Stiftung is hereby gratefully acknowledged.

REFERENCES

1. For general references, see: (a) *Comprehensive Organometallic Chemistry, II*, E. W. Abel, F. G. A. Stone, G. Wilkinson (Eds.), Vol. 1, Chap. 6–8.9, Elsevier Science, Oxford (1995); (b) N. S. Hosmane and J. A. Maguire, in *Electron-Deficient Boron and Carbon Clusters*, G. A. Olah, K. Wade, R. E. Williams (Eds.), Chap. 9, pp. 215–235, Wiley, N.Y. (1991); (c) N. S. Hosmane and J. A. Maguire. *Adv. Organomet. Chem.* **30**, 99–150 (1990).
2. (a) A. K. Saxena, J. A. Maguire, N. S. Hosmane. *Chem. Rev.* **97**, 2421–2462 (1997) and references therein; (b) N. S. Hosmane, K.-J. Lu, H. Zhang, J. A. Maguire. *Organometallics* **16**, 5163–5170 (1997); (c) N. S. Hosmane, J. Yang, K.-J. Lu, H. Zhang, U. Siriwardane, M. S. Islam, J. L. C. Thomas, J. A. Maguire. *Organometallics* **17**, 2784–2796 (1998).
3. (a) N. S. Hosmane, Y. Wang, H. Zhang, K.-J. Lu, J. A. Maguire, T. G. Gray, K. A. Brooks, E. Waldhör, W. Kaim, R. K. Kremer. *Organometallics* **16**, 1365–1377 (1997); (b) H. Zhang, Y. Wang, A. K. Saxena, A. R. Oki, J. A. Maguire, N. S. Hosmane. *Organometallics* **12**, 3933–3944 (1993); (c) C. J. Thomas, J. Lei, H. Zhang, U. Siriwardane, J. A. Maguire, V. P. Weiss, K. A. Brooks, N. S. Hosmane. *Organometallics* **14**, 1365–1376 (1995).
4. (a) N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang, D. Zhu, E. M. McDonald, J. A. Maguire. *Phosphorus, Sulfur, Silicon* **93–94**, 253 (1994) and references therein; (b) N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang, J. A. Maguire. *Organometallics* **15**, 626–638 (1996); (c) N. S. Hosmane, Y. Wang, H. Zhang, J. A. Maguire, M. McInnis, T. G. Gray, J. D. Collins, R. K. Kremer, H. Binder, E. Waldhör, Kaim. *Organometallics* **15**, 1006–1013 (1996).
5. Edwards Air Force Base RTS Aug/Sept 1999 Bulletin entitled "Pentaborane: (http://www.edwards.af.mil/penvmng/NewsInfo/RTS/1999RTS/AugSep99/augsep99p5.htm), Air Force Closes Book on Old Exotic Rocket Fuel", and references therein.
6. M. G. H. Wallbridge and C. G. Savory. *J. Chem. Soc., Dalton Trans.* 179–184 (1973).
7. N. S. Hosmane, J. R. Wermer, H. Zhu, T. D. Getman, S. G. Shore. *Inorg. Chem.* **26**, 3638–3639 (1987).
8. (a) R. L. Middaugh. In *"Boron Hydride Chemistry",* E. L. Muetterties (Ed.), Chap. 8, pp. 273–300, Academic Press, New York (1975); (b) S. G. Shore. In *Clusters, Rings and Polymers of the Main Group Elements,* A. H. Cowley (Ed.), Chap. 1, ACS Symposium Series, American Chemical Society, Washington, DC (1983); (c) S. H. Lawrence, J. R. Wermer, S. K. Boocock, M. A. Banks, P. C. Keller, S. G. Shore. *Inorg. Chem.* **25**, 367–372 (1986).
9. M. A. Toft, J. B. Leach, F. L. Himpsl, S. G. Shore. *Inorg. Chem.* **21**, 1952–1957 (1982).
10. Natural and ^{10}B-enriched decaborane ($B_{10}H_{14}$), and *iso*-$B_{18}H_{22}$ are commercially available by KATCHEM LTD., Czech Republic, for the price per gram of \$15, \$250, \$151, and \$510, respectively.
11. H. I. Schlesinger, H. C. Brown, D. L. Mayfield, J. R. Gilbreath. *J. Am. Chem. Soc.* **75**, 213–215 (1953).
12. H. I. Schlesinger, H. C. Brown, A. E. Finholt. *J. Am. Chem. Soc.* **75**, 205–209 (1953).
13. K. C. Nainan and G. E. Ryschkewitsch. *Inorg. Nucl. Chem. Lett.* **6**, 765–766 (1970); G. E. Ryschkewitsch and K. C. Nainan. *Inorg. Synth.* **15**, 111–118 (1974).
14. L. Adams, S. N. Hosmane, J. E. Eklund, J. Wang, N. S. Hosmane. *J. Am. Chem. Soc.* **124**, 7292–7293 (2002).

15. L. V. McCarty and P. A. Di Giorgio. *J. Am. Chem. Soc*. **73**, 3138–3143 (1951).
16. (a) G. E. Ryschkewitsch and V. R. Miller. *J. Am. Chem. Soc.* **97**, 6258–6259 (1975); (b) V. R. Miller and G. E. Ryschkewitsch. *Inorg. Synth.* **15**, 118–122 (1974); (c) N. S. Hosmane and R. N. Grimes. *Inorg. Chem.* **18**, 3294–3297 (1979).
17. (a) A. H. Soloway, W. Tjarks, B. A. Bauman, F. G. Rong, R. F. Barth, I. M. Codogni, J. G. Wilson. *Chem. Rev.* **98**, 1515–1562 (1998); (b) *Advances in Neutron Capture Therapy, Vol. II, Chemistry and Biology,* B. Larsson, J. Crawford, R. Weinreich (Eds.), Elsevier Science B. V., Amsterdam (1997).
18. (a) L. Adams, S. Tomlinson, J. Wang, S. N. Hosmane, J. A. Maguire, N. S. Hosmane. *Inorg. Chem. Commun.* **5**, 765–767 (2002); (b) C. T. Brewer and R. N. Grimes. *J. Am. Chem. Soc.* **107**, 3552–3557 (1985).
19. L. I. Zakharkin and L. S. Podvisotskaya. *Zh. Obshch. Khim.* **37**, 506 (1967); L. I. Zakharkin, V. N. Kalinin, L. S. Podvisotskaya. *Izv. Akad. Nauk SSSR, Ser. Khim.* 2310 (1967); V. I. Stanko, Yu. V. Goltyapin, V. A. Brattsev. *Zh. Obshch. Khim.* **39**, 1175 (1969).
20. N. S. Hosmane, L. Jia, H. Zhang, J. W. Bausch, G. K. S. Prakash, R. E. Williams, T. P. Onak. *Inorg. Chem.* **30**, 3793–3795 (1991).
21. M. B. Ezhova, H. Zhang, J. A. Maguire, N. S. Hosmane. *J. Organomet. Chem.* **550***,* 409–422 (1998).
22. N. S. Hosmane, D. Zhu, J. E. McDonald, H. Zhang, J. A. Maguire, T. G. Gray, S. C. Helfert. *Organometallics* **17**, 1426–1437 (1998).
23. N. S. Hosmane, D. Zhu, H. Zhang, A. R. Oki, J. A. Maguire. *Organometallics* **17**, 3196–3203 (1998).
24. C. Zheng, J.-Q. Wang, J. A. Maguire, N. S. Hosmane. *Main Group Met. Chem.* **22**, 361–366 (1999).
25. N. S. Hosmane. *J. Organomet. Chem.* **581**, 13–27 (1999).
26. N. S. Hosmane. *Current Sci.* **78**, 475–486 (2000).
27. G. Rana, J. A. Maguire, S. N. Hosmane, N. S. Hosmane. *Main Group Met. Chem.* **23**, 527–547 (2000).
28. N. S. Hosmane, S.-J. Li, C. Zheng, J. A. Maguire. *Inorg. Chem. Commun.* **4**, 104–107 (2001).
29. N. S. Hosmane, H. Zhang, J. A. Maguire, T. Demissie, A. R. Oki, A. K. Saxena, W. N. Lipscomb. *Main Group Met. Chem.* **24**, 589–596 (2001).
30. J. Wang, S.-J. Li, C. Zheng, J. A. Maguire, N. S. Hosmane. *Organometallics* **21**, 3314–3316 (2002).
31. J. Wang, S.-J. Li, C. Zheng, J. A. Maguire, N. S. Hosmane. *Inorg. Chem. Commun.* **5**, 602–605 (2002).
32. J. Wang, S.-J. Li, C. Zheng, J. A. Maguire, N. S. Hosmane. *Angew. Chem., Int. Ed. Engl.* (2002). Submitted for publication.
33. E. Wiberg, O. Stecher, H. J. Andraschek, L. Kreuzbichler, E. Staude. *Angew. Chem., Int. Ed. Engl.* **2**, 507 (1963); C. Eaborn, R. A. Jackson, R. W. Walsingham. *J. Chem. Soc. C* 2188–2191 (1967); J. L. Wardell. *Comp. Organomet. Chem.* **1**, 52–54 (1982); D. C. Billington. *Comp. Org. Syn.* **3**, 413–434 (1991).
34. Special volume: *From Borane Cages to Metal Clusters: Recent Developments*, T. P. Fehlner and N. S. Hosmane (Guest Eds.). *J. Organomet. Chem.* **614–615**, 1–333 (2000); Z. Xie. *Coord. Chem. Rev*. **231**, 23–46 (2002).
35. Y. Zhu, K. Vyakaranam, J. A. Maguire, W. Quintana, F. Teixidor, C. Vinas, N. S. Hosmane. *Inorg. Chem. Commun.* **4**, 486–489 (2001).
36. Y. Zhu, J. A. Maguire, N. S. Hosmane. *Inorg. Chem. Commun.* **5**, 296–299 (2002).
37. J. A. Maguire, J.-Q. Wang, C. Zheng, C. Li, N. S. Hosmane. *Inorg. Chim. Acta* **334C**, 91–104 (2002).

38. J. Wang, Y. Zhu, S.-J. Li, C. Zheng, J. A. Maguire, N. S. Hosmane. *J. Organomet. Chem.* (2003). In press.
39. M. Westerhausen, C. Gückel, S. Schneiderbauer, H. Nöth, N. S. Hosmane. *Angew. Chem., Int. Ed.* **40**, 1902–1904 (2001).
40. M. Bremer, H. Nöth, M. Thomann, M. Schmidt. *Chem. Ber.* **128**, 455–460 (1995).
41. M. Westerhausen, C. Gückel, T. Habereder, M. Vogt, M. Warchhold, H. Nöth. *Organometallics* **20**, 893–899 (2001).
42. (a) P. Jutzi. *J. Organomet. Chem*. **400**, 1–17 (1990); (b) T. P. Hanusa. *Chem. Rev*. **93**, 1023–1036 (1993); (c) D. J. Burkey and T. P. Hanusa. *Comments Inorg. Chem*. **17**, 41–47 (1995); (d) P. Jutzi. *Chem. Rev*. **99**, 969–990 (1999).
43. R. Khattar, C. B. Knobler, M. F. Hawthorne. *J. Am. Chem. Soc*. **112**, 4962–4963 (1990).
44. R. Khattar, C. B. Knobler, M. F. Hawthorne. *Inorg. Chem*. **29**, 2191–2192 (1990).
45. N. S. Hosmane, D. Zhu, J. E. McDonald, H. Zhang, J. A. Maguire, T. G. Gray, S. C. Helfert. *J. Am. Chem. Soc*. **117**, 12362–12363 (1995).
46. M. Westerhausen, C. Gückel, S. Schneiderbauer, H. Nöth, N. S. Hosmane. To be published.