Monocarboranes

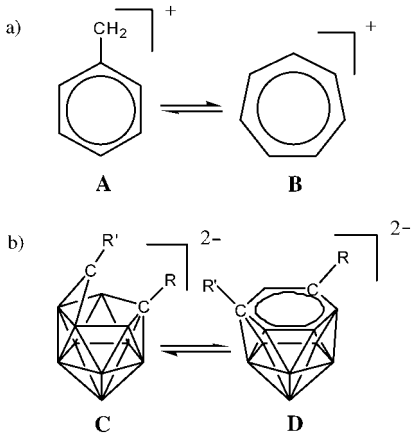
Carbon Extrusion in 1,2-Dicarba-*closo*-dodecaboranes: Regioselective Boron Substitution in Ten-Vertex *closo*-Monocarbaborane Anions**

*Anna Laromaine, Francesc Teixidor, and Clara Viñas**

Dedicated to Dr. Raikko Kivekäs on the occasion of his 60th birthday

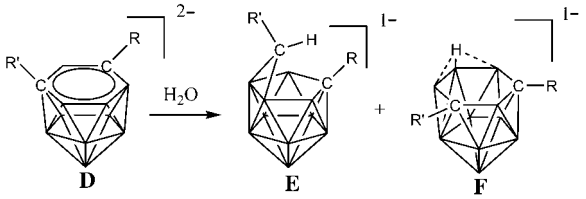
While dicarba-*closo*-dodecaboranes are the most investigated of polyhedral boron-containing clusters,[1,2] *closo*-monocarbaboranes have been less examined,[1] probably because of the absence of suitable protocols of synthesis. Currently, the monocarbaboranes [1-*closo*-CB_9H_{10}]$^-$ and [1-*closo*-$CB_{11}H_{12}$]$^-$ along with their derivatives are attracting much attention.[3,4] This has stimulated the search for new methods of synthesis; [1-*closo*-CB_9H_{10}]$^-$ was originally obtained from $B_{10}H_{14}$ and CN^- but is now more conveniently produced from [6-(NMe_3)-*nido*-6-CB_9H_{11}] by dehydrogenation.[5] The method of Brellochs,[6] based on the reaction of RCHO with *arachno*-$B_{10}H_{14}$, is gaining importance for the synthesis of phenyl derivatives of [1-*closo*-CB_9H_{10}]$^-$.[4,7] Ultimately all these methods are based on a single carbon insertion into a $B_{10}H_{14}$ cluster followed by a deboronation step. In theory, an alternative way to the [1-*closo*-CB_9H_{10}]$^-$ cluster would be from the highly stable and widely studied 1,2-dicarba-*closo*-dodecaboranes, namely, carbon extrusion with subsequent boron elimination. This is the objective of this work.

Taking the well-known benzyl cation–tropylium ion rearrangement as a model (Scheme 1 a),[8] Jemmis and Jayasree have carried out theoretical calculations on the rearrangement of the dicarbaboranyl methyl cation to generate tricarbaborane cations.[9] We considered that a monocarbaborane could be produced from a dicarbaborane by a similar extrusion of one cluster carbon atom. The analogy between the system in boron chemistry and the benzyl cation–tropylium equilibrium is shown in Scheme 1 b.



Scheme 1. Schematic representations of a) the benzyl cation–tropylium rearrangement and b) the rearrangement of the 12-vertex dicarba-*nido*-dodecaborate(-2).

Although there is no experimental proof for the expected rearrangement, support comes from the fact that isomer **E** (Scheme 2), which is structurally similar to **C** (Scheme 1), is produced on treatment of **D** with water. A second isomer **F** (less stable than **E** by 6.7 kcal mol^{-1}) is also produced.[10] Indeed **F** was considered to be the only reactive isomer,[11,12] and pioneering work for carbon extrusion from **F** has been reported[11c,13] in which a mixture of non-*closo* compounds forms depending on the nucleophile. To our understanding, the reactive nature of **F** as well as its easily accessible C_2B_4 open face facilitated formation of a range of products. It was



Scheme 2. Protonation of [$C_2B_{10}RR'H_{10}$]$^{2-}$ produces the two isomers [7-R-μ-(9,10-HR'C)-7-*nido*-$CB_{10}H_{11}$]$^-$ (**E**) and [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{11}$]$^-$ (**F**).

[*] A. Laromaine, Prof. F. Teixidor, Dr. C. Viñas
Institut de Ciència de Materials de Barcelona (CSIC)
Campus UAB
08193 Bellaterra (Spain)
Fax: (+34) 93-580-57-29
E-mail: clara@icmab.es

[**] The authors thank the CICYT (MAT01-1575) and the Generalitat de Catalunya (2001/SGR/00337) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200462209

anticipated that the more rigid structure of **E** would be more likely to undergo a regioselective reaction.

Two drawbacks were apparent: Isomer **E** had been synthesized in low yield, around 20%,[11b] and had been considered to be unreactive.[11,12] Recently a convenient route to **E** with Mg as a reducing agent has been described with yields close to 95% for R = H, Me, Ph.[14] As far as the low reactivity of **E** was concerned, we have recently shown that it can be forced to react with $[PdCl_2(PPh_3)_2]$ to generate a mixture of compounds, mostly obtained in low yield.[15] Although some products were generated by carbon extrusion, no [1-*closo*-CB_9H_{10}]$^-$ derivatives were found. In order to generate the latter, a regioselective cluster deboronation on **E** was of utmost importance, and we found K[NC_4H_4] and K[$NC_4Me_2H_2$] to be the most suitable nucleophiles for this task.[16a]

In a typical experiment, [NMe_4][μ-(9,10-H_2C)-7-*nido*-$CB_{10}H_{11}$] (**E**, R = H; 0.12 mmol) in 20 mL of THF was added to freshly prepared K[NC_4H_4] (0.48 mmol) under N_2. The mixture was heated at reflux for 72 h. The reaction was monitored by $^{11}B\{^1H\}$ NMR spectroscopy to examine the appearance of a resonance near +30 ppm. Following workup of the products, [NMe_4][6-Me-1-*closo*-CB_9H_9] was obtained in 55% yield.

This product was characterized by ^{11}B, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, and $^1H\{^{11}B\}$ NMR spectroscopy and MALDI-TOF analysis. A pattern 1(d):1(s):2(d):2(d):2(d):1(d) at δ = 30.3, −16.2, −17.1, −18.2, −22.2, and −26.5 ppm, respectively, in agreement with a six-substituted bicapped square antiprism,[17] was observed in the $^{11}B\{^1H\}$ NMR spectrum. Comparison with resonances for [1-*closo*-CB_9H_{10}]$^-$, application of ^{11}B NMR rules[18] for *closo* species, and the position of the singlet at δ = −16.2 ppm indicated that a regioselective alkyl substitution at the 6-position in [1-*closo*-CB_9H_{10}]$^-$ had taken place from the readily available 1,2-*closo*-$C_2B_{10}H_{12}$ neutral compounds. The assignments indicated on the $^{11}B\{^1H\}$–$^{11}B\{^1H\}$ 2D COSY NMR spectrum in Figure 1 are consistent with the structure of [6-Me-1-*closo*-CB_9H_9]$^-$: B10 is correlated with B6, B{7,9}, and B8; B8 is correlated with B10, B{7,9}, and B{4,5}; B{7,9} is correlated with B10, B8, B6, B{4,5}, and B{2,3}. The MALDI-TOF mass spectrum of [6-Me-1-*closo*-CB_9H_9]$^-$ (Figure 2) displays a signal group centered at *m*/*z* 133.2 corresponding to the anionic fragment. All this data prove that [1-R-6-CH_2R′-1-*closo*-CB_9H_8]$^-$ derivatives can be generated in only two steps. [6-Me-1-*closo*-CB_9H_9]$^-$ is the first example of a monoalkyl substitution on B in [1-*closo*-CB_9H_{10}]$^-$ derivatives.

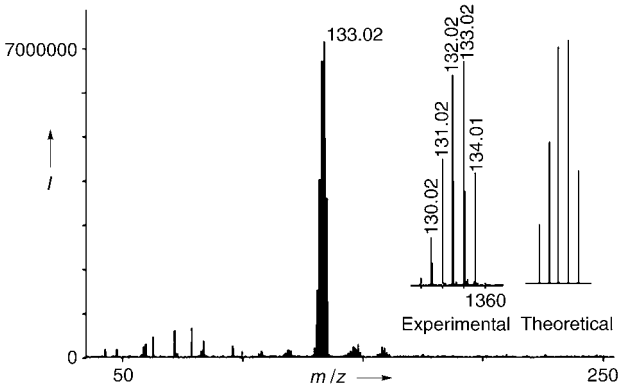


Figure 2. The MALDI-TOF mass spectrum of [NMe_4]-**1** with a comparison of the theoretical and experimental distribution for the molecular peak. *I* = intensity.

To demonstrate the versatility of this reaction, it was also applied to 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$, 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, and 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. In all cases anions corresponding to [1-R-6-CH_2R′-1-*closo*-CB_9H_8]$^-$ were obtained (Table 1).

Table 1: Nonoptimized yields for the synthesis of [1-R-6-CH_2R′-1-*closo*-CB_9H_8]$^-$.

Compound	[1-R-6-CH_2R′-1-*closo*-CB_9H_8]$^-$		
	R	R′	Yield [%]
[NMe_4]-**1**	H	H	55
[NBu_4]-**2**	H	Me	30
[NBu_4]-**3**	Me	Me	47
[NBu_4]-**4**	H	Ph	45

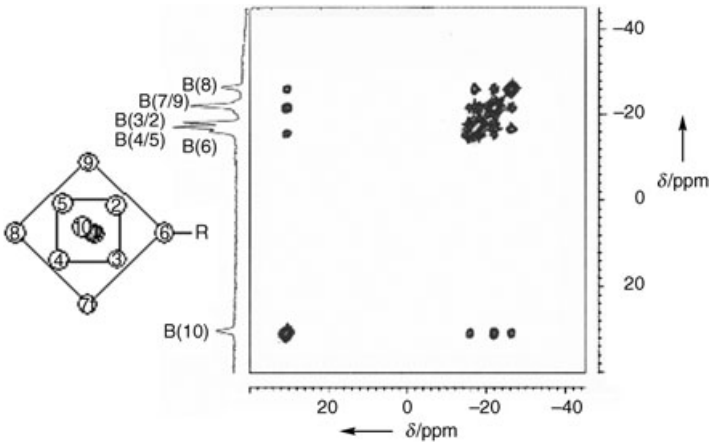
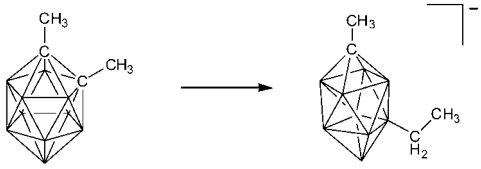


Figure 1. The $^{11}B\{^1H\}$–$^{11}B\{^1H\}$ 2D COSY NMR spectrum of [NMe_4]-**1** with the assignments deduced from the off-diagonal resonances.

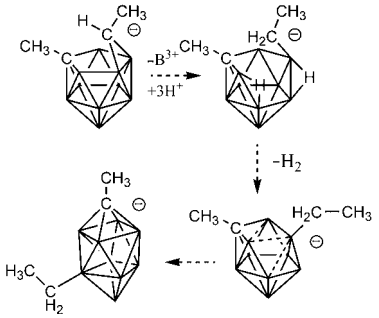
In Scheme 3 the transformation from the neutral dicarbaborane to the anionic monocarbaborane cluster is exemplified for [1-Me-6-Et-1-*closo*-CB_9H_8]$^-$. Considering that carbon extrusion takes place, the alkyl group at the 6-position must have one more carbon atom than in the precursor dicarbaborane. As an



Scheme 3. Schematic representation of the carbon extrusion for regioselective synthesis of [1-Me-6-Et-1-*closo*-CB_9H_9]$^-$ from [1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$] species.

example, if [6-Pr-1-*closo*-CB_9H_9]$^-$ were sought, 1-Et-1,2-*closo*-$C_2B_{10}H_{11}$ would be required as the starting compound.

A plausible pathway for the synthesis of **3**$^-$ is shown in Scheme 4. A B^{3+} unit is formally removed from [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$ by using [NC_4H_4]$^-$. At this stage the nonclassical bridging carbon atom of μ-(9,10-HMeC) is converted into a classical one. The boron atom removed is B(9) or B(10), generating a six-membered open face. Dehydrogenation leads to the *closo* monocarbaborane anion. The deboronation step is very important in this synthetic process. In previous work,[15] a neutral nucleophile (PPh_3) was shown to attack the bridging μ-(9,10-HMeC) group to generate the CH(Me)PPh_3 moiety. The result was a nucleophilic addition. The negative [NC_4H_4]$^-$ removes B(9) or B(10) to produce a *closo* {CB_9} anionic cluster and $(H_4C_4N)_3$B-THF.[16b] As the deboronation succeeded with an anionic nucleophile, experiments were also carried out with CN^- and F^- on [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$. For CN^-, [1-Me-6-Et-1-*closo*-CB_9H_8]$^-$ was formed in yields of less than 3%, and with F^- the starting material was fully recovered. The effect of enhanced nucleophilicity was monitored by ^{11}B NMR spectroscopy using [$NC_4Me_2H_2$]$^-$. Interestingly the same conversion as for [NC_4H_4]$^-$ (55%) was obtained in 24 h (72 h for [NC_4H_4]$^-$).



Scheme 4. Suggested pathway for deboronation and carbon extrusion in the [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$.

The inadequacy of isomer **F** (Scheme 2) for this reaction was demonstrated by attempting to produce **1**$^-$ under the same conditions and with K[$NC_4Me_2H_2$] as a nucleophile. In this case **1**$^-$ was produced in only 2% yield, along with [NMe_4][7,8-*nido*-$C_2B_9H_{11}$] (21%) and 1,2-*closo*-$C_2B_{10}H_{12}$ (58%). Even the low yield of **1**$^-$ cannot be claimed to originate from the use of **F** because the latter slowly isomerizes under the reaction conditions to yield **E**, which in turn may generate the [6-Me-1-*closo*-CB_9H_9]$^-$ cluster.

With these results we have shown that [1-H-6-CH_2R′-1-*closo*-CB_9H_8]$^-$ (R′ = H, Me, Ph) or [1-Me-6-CH_2Me-1-*closo*-CB_9H_8]$^-$ derivatives can be produced in a regioselective way from 1-H-2-R′-1,2-*closo*-$C_2B_{10}H_{10}$ (R′ = H, Me, Ph) or 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$. Work is now underway for the case of unsymmetrical alkyl/aryl substitution on both cluster carbon atoms in the dicarbaboranes, to discern which group will occupy the 6-position in the resulting [1-*closo*-CB_9H_{10}]$^-$ derivatives, and which functional groups are compatible with such rearrangements.

Received: October 5, 2004
Revised: December 20, 2004
Published online: March 10, 2005

Keywords: boron · carboranes · rearrangement · regioselectivity · synthetic methods

[1] B. Stíbr, *Chem. Rev.* **1992**, *92*, 225.
[2] V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209.
[3] a) Z. Xie, T. Jelinek, R. Bau, C. Reed, *J. Am. Chem. Soc.* **1994**, *116*, 1907; b) C. Reed, *Acc. Chem. Res.* **1998**, *31*, 133; c) S. Strauss, *Chem. Rev.* **1993**, *93*, 927; d) B. T. King, Z. Janousek, B. Grüner, M. Trammell, B. C. Noll, J. Michl, *J. Am. Chem. Soc.* **1996**, *118*, 3313.
[4] P. Kaszynski, *Collect. Czech. Chem. Commun.* **1999**, *64*, 895, and references therein.
[5] a) K. Nestor, B. Stíbr, J. D. Kennedy, M. Thornton-Pett, T. Jelinek, *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262; b) T. Jelinek, B. Stíbr, J. Plesek, M. Thornton-Pett, J. D. Kennedy, *J. Chem. Soc. Dalton Trans.* **1997**, 4231.
[6] B. Brellochs in *Contemporary Boron Chemistry* (Eds.: M. G. Davidson, A. K. Hughes, T. B. Marder, K. Wade), Royal Society of Chemistry, Cambridge, **2000**, pp. 212.
[7] a) J. Plesek, T. Jelinek, B. Stíbr, S. Hemánek, *J. Chem. Soc. Chem. Commun.* **1988**, 348; b) T. Jelinek, B. Stíbr, J. Plesek, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* **1995**, 431.
[8] a) A. Nicolaides, L. Radom, *J. Am. Chem. Soc.* **1994**, *116*, 9769; b) S. K. Shin, *Chem. Phys. Lett.* **1997**, *280*, 260; c) C. Lifshitz, *Acc. Chem. Res.* **1994**, *27*, 138; d) C.-H. Shin, K-C. Park, S.-J. Kim, B. Kim, *Bull. Korean Chem. Soc.* **2002**, *23*, 337.
[9] E. D. Jemmis, E. G. Jayasree, *Inorg. Chem.* **2003**, *42*, 7725.
[10] M. L. McKee, M. Bühl, P. von R. Schleyer, *Inorg. Chem.* **1993**, *32*, 1712.
[11] a) G. B. Dunks, R. J. Wiersema, M. F. Hawthorne, *J. Chem. Soc. Chem. Commun.* **1972**, 899; b) G. B. Dunks, R. J. Wiersema, M. F. Hawthorne, *J. Am. Chem. Soc.* **1973**, *95*, 3174; c) J. Plesek, T. Jelinek, B. Stíbr, S. Hermánek, *J. Chem. Soc. Chem. Commun.* **1988**, 348.
[12] a) D. Grafstein, J. Dvorak, *Inorg. Chem.* **1963**, *2*, 1128; b) L. Zakharkin, V. Kalinin, L. Podvisotskaya, *Izv. Akad. Nauk SSSR Ser. Khim.* **1967**, *10*, 2310; c) Y. Stanko, V. Goltypin, V. Brattsev, *Zh. Obshch. Khim.* **1969**, *39*, 1175.
[13] J. Plesek, B. Stíbr, X. L. R. Fontaine, T. Jelinek, M. Thornton-Pett, S. Hermánek, J. D. Kennedy, *Inorg. Chem.* **1994**, *33*, 2994.
[14] C. Viñas, G. Barberà, F. Teixidor, *J. Organomet. Chem.* **2002**, *642*, 16.
[15] J. Bould, A. Laromaine, C. Viñas, F. Teixidor, L. Barton, N. P. Rath, R. E. K. Winter, R. Kivekäs, R. Sillanpää, *Organometallics* **2004**, *23*, 3335.
[16] a) M. Lamrani, S. Gómez, C. Viñas, F. Teixidor, R. Sillanpää, R. Kivekäs, *New J. Chem.* **1996**, *20*, 909; b) F. Teixidor, S. Gómez, M. Lamrani, C. Viñas, R. Sillanpää, R. Kivekäs, *Organometallics* **1997**, *16*, 1278.
[17] a) S. V. Ivanov, J. J. Rockwell, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *Inorg. Chem.* **1996**, *35*, 7882; b) N. J. Bullen, A. Franken, C. A. Kilner, J. D. Kennedy, *Chem. Commun.* **2003**, 1684.
[18] F. Teixidor, C. Viñas, R. W. Rudolph, *Inorg. Chem.* **1986**, *25*, 3339.

