J|A|C|S
COMMUNICATIONS

Role of C,C′-Linkage in the Formation and Stabilization of Supercarboranes. Synthesis and Structure of Carbon-Atoms-Apart 13-Vertex Carborane and 14-Vertex Metallacarborane

Jian Zhang, Liang Deng, Hoi-Shan Chan, and Zuowei Xie*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

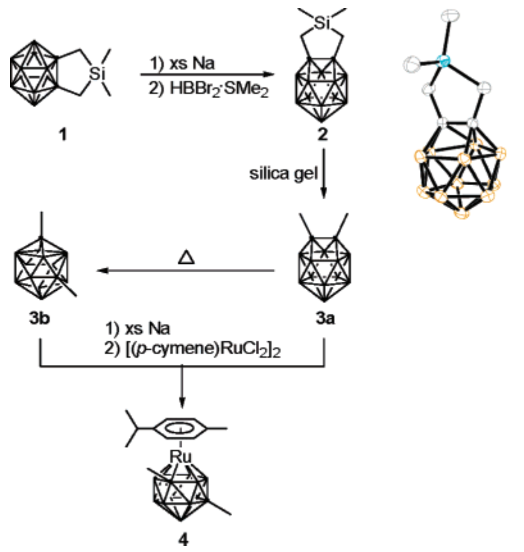
Received October 5, 2006; E-mail: zxie@cuhk.edu.hk

It is only in recent years that significant progress been made in the chemistry of supercarboranes.[1−5] Carbon-atoms-adjacent (CAd) 13- and 14-vertex carboranes[1−3] and their corresponding 14- and 15-vertex metallacarboranes[3−5] have been successfully prepared and structurally characterized. Such a breakthrough relies on the use of CAd carborane anions as starting materials. The methodology for the controlled syntheses of CAd *nido*-carboranes and *arachno*-carboranes developed earlier in our laboratory provides a very important entry point to supercarboranes.[6−8] It is very clear that the short C,C′-linkage can force the two cage carbon atoms of carboranes in adjacent positions during the reductive process.[6−8] Is such a linkage necessary to stabilize the supercarboranes? There is no unambiguous answer yet. Nonetheless, there have been some intriguing hints. When the Welch group treated the carbon-atoms-apart (CAp) *nido*-$C_2B_{10}H_{12}^{2-}$ with BI_3, the isolated product was 3-I-1,2-$C_2B_{10}H_{11}$, which suggested successful initial formation of a 13-vertex carborane that spontaneously degraded by loss of a BH group.[1] This result led to an assumption that the C,C′-linkage was crucial to stabilize the 13-vertex carborane. Therefore, we initiated a program to study the role of such a C,C′-linkage in the formation and stabilization of supercarboranes.

Reaction of 1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (**1**)[9] with excess Na metal at room temperature, followed by treatment with 2 equiv of $HBBr_2{\cdot}SMe_2$ in toluene/CH_2Cl_2, gave, after recrystallization, the 13-vertex carborane 1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{11}H_{11}$ (**2**) in 39% isolated yield (Scheme 1).[10] It was fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy as well as high-resolution mass spectrometry (HRMS). The ^{11}B NMR spectrum showed a 1:10 pattern. Two singlets at 2.55 and 0.31 ppm attributable to the methylene and methyl units, respectively, were observed in the ^1H NMR spectrum. Single-crystal X-ray analyses[10] confirmed that **2** has a henicosahedral structure which is similar to that of known 13-vertex carboranes.[1−3]

Compound **2** is stable in air for several weeks in the solid state. Its $CDCl_3$ solution is, however, not very stable, and a new species was observed in the ^{11}B NMR spectra after 10 days. Such a process was sped up after adding a small amount of silica gel, which finally led to a single product as indicated by the ^{11}B NMR spectra. This incident spurred us to investigate this reaction in detail. After many attempts, a simple desilylation procedure was developed. Compound **2** was subjected to column chromatography on SiO_2 using *n*-hexane as elute,[11] affording 1,2-Me_2-1,2-$C_2B_{11}H_{11}$ (**3a**) and its CAp isomer $Me_2C_2B_{11}H_{11}$ (**3b**) in 60 and 30% yields, respectively.[10] Compound **3a** can be quantitatively converted into **3b** upon heating in the toluene solution, suggesting that **3b** results from **3a**[12] and is a thermodynamically stable product. No decomposition was observed during this process as evidenced by NMR spectra. These results show clearly that the C,C′-linkage does not have any obvious effects on the stability of 13-vertex carboranes.

Scheme 1. Indirect Synthetic Routes to CAp 13-Vertex Carboranes and 14-Vertex Metallacarborane



Compounds **3a** and **3b** have the identical HRMS, indicating that they are isomers. The ^{11}B NMR spectrum of **3a** showed a clear 1:5:5 pattern, while that of **3b** exhibited a pseudo 1:10 pattern where a broad peak is not well resolved. The ^1H NMR spectra displayed only one singlet of the methyl protons at 2.73 ppm for **3a** and two singlets at 2.63 and 1.89 ppm assignable to the two different methyl groups for **3b**. Accordingly, two resonances at 140.6 (cage *C*) and 34.8 ppm (*C*H_3) and four peaks at 120.7, 83.0 (cage *C*) and 35.6, 27.3 ppm (*C*H_3) were observed in the ^{13}C NMR spectra of **3a** and **3b**, respectively. These spectroscopic data suggest that the two cage carbon atoms in **3b** have different coordination environments: one may be more connected than the other. The molecular structure of **3a** was confirmed by single-crystal X-ray analyses,[10] as shown in Figure 1. The cage geometry is almost the same as that observed in **2** with the two cage carbon atoms remaining in adjacent positions. Compound **3a** represents the first 13-vertex carborane without a C,C′-linkage.

The above experimental results show that **3b** is thermodynamically more stable than its structural isomer **3a**, which is well consistent with the properties of 12-vertex carboranes.[13] This important finding prompted us to re-examine the reaction of CAp *nido*-$C_2B_{10}H_{12}^{2-}$ with RBX_2 reagent. Treatment of 1,2-Me_2-1,2-$C_2B_{10}H_{10}$ (**5**)[14] with excess Na in the presence of a catalytic amount of naphthalene giving CAp [7,9-Me_2-7,9-$C_2B_{10}H_{10}$]Na_2, followed by reaction with 2 equiv of $HBBr_2{\cdot}SMe_2$ in toluene/CH_2Cl_2, gave, after chromatographic separation, **3b** and **5** in 5 and 17% isolated yields, respectively (Scheme 2).[10] The remaining product is a mixture of inseparable highly polar boron-containing species.

10.1021/ja067129e CCC: $37.00 © 2007 American Chemical Society

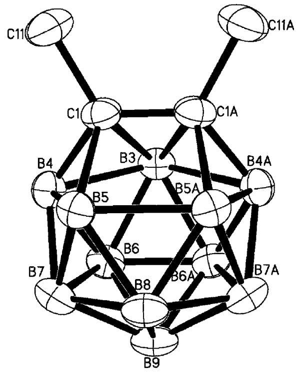
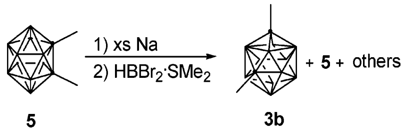


Figure 1. Molecular structure of 1,2-Me_2-1,2-$C_2B_{11}H_{11}$ (**3a**). Selected bond lengths [Å]: C1−C1A 1.421(5), C1−C11 1.520(3), C1−B3 1.892(4), C1−B4 1.600(4), C1−B5 1.800(3).

Scheme 2. Direct Synthesis of CAp 13-Vertex Carborane



Although the synthetic yield is rather low, this is the first report to show that CAp 13-vertex carborane can be directly prepared via capitation reaction of [*nido*-7,9-R_2-7,9-$C_2B_{10}H_{10}$]Na_2 with a dihaloborane reagent. In view of this result and spectroscopic data of **3a** and **3b**, it is reasonable to assume that the two cage carbon atoms in **3b** remain in *meta* positions after the capitation reaction, giving a thermodynamically more stable all-triangulated docosahedral structure with the cage carbons being likely located in the 1,6-positions, that is, 1,6-Me_2-1,6-$C_2B_{11}H_{11}$.

Both **3a** and **3b** were readily reduced by excess sodium in the absence of naphthalene to give the corresponding sodium salts with distinct ^{11}B NMR spectra. A 1:5:5 pattern in the range of −9.2 to −26.0 ppm was observed in the ^{11}B NMR spectrum of [**3a**]Na_2, which is very similar to that observed in CAd [*nido*-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$],[3] suggesting that the two cage carbon atoms still remain adjacent. The ^{11}B NMR spectrum of [**3b**]Na_2 exhibited a 1:2:2:2:2:2 pattern within −2.7 to −33.1 ppm. Both salts were treated with 0.5 equiv of [(*p*-cymene)$RuCl_2$]$_2$ in THF to generate the same 14-vertex ruthenacarborane 2,9-Me_2-1-(*p*-cymene)-1,2,9-$RuC_2B_{11}H_{11}$ (**4**) in 19% (from **3a**) and 75% yields (from **3b**), respectively (Scheme 1).[10] In addition, 60% of **3a** was recovered from the former reaction. An initial formation of 2,3-Me_2-1-(*p*-cymene)-1,2,3-$RuC_2B_{11}H_{11}$ might be suggested when using **3a** as the starting material, which subsequently isomerizes into the thermodynamically stable product **4**.[15]

Complex **4** was fully characterized by ^1H, ^{13}C, ^{11}B NMR, and HRMS as well as single-crystal X-ray analyses. It adopts a bicapped hexagonal antiprism geometry as that of 2,8-$(CH_2)_3$-1-(*p*-cymene)-1,2,8-$RuC_2B_{11}H_{11}$[5] with a Ru atom occupying one of the apical vertices, two cage carbons seating on the two hexagonal belts, and being separated by one boron atom (Figure 2). The Ru−CB_5(cent) distance of 1.41 Å and Ru−C_6(cent) distance of 1.77 Å are very close to the corresponding values of 1.40 and 1.77 Å observed in 2,8-$(CH_2)_3$-1-(*p*-cymene)-1,2,8-$RuC_2B_{11}H_{11}$.[5]

In conclusion, we have synthesized, for the first time, both CAd and CAp 13-vertex carboranes and 14-vertex metallacarborane without any C,C′-linkages using direct and indirect methods. The results show that the C,C′-linkages do not have any obvious effect on the thermal and kinetic stability of 13-vertex carboranes, and the CAp isomer is thermodynamically more stable than the CAd one. The role of the linkages is just to lower the reducing power of the *nido*-carborane dianions,[7] facilitating the capitation reaction.[2] CAp 13-vertex carboranes can be directly prepared by the reaction of [*nido*-7,9-R_2-7,9-$C_2B_{10}H_{10}$]Na_2 with dihaloborane reagents. However, the yield is rather low due to the very strong reducing power of the CAp *nido*-carborane dianions. This work supports our earlier argument that the prevention of the redox reactions is the key to obtaining successively larger carboranes.[2]

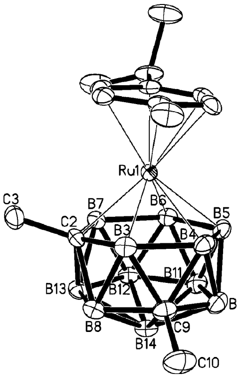


Figure 2. Molecular structure of 2,9-Me_2-1-(*p*-cymene)-1,2,9-$RuC_2B_{11}H_{11}$ (**4**). Selected bond lengths [Å]: Ru1−C2 2.247(3), Ru1−B3 2.194(4), Ru1−B4 2.235(4), Ru1−B5 2.275(4), Ru1−B6 2.279(4), Ru1−B7 2.265(4).

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administration Region (Project No. 403906).

Supporting Information Available: Detailed experimental procedures, characterization data, and X-ray data for **2**, **3a**, and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Burke, A.; Ellis, D.; Giles, B. T.; Hodson, B. E.; Macgregor, S. A.; Rosair, G. M.; Welch, A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 225−228.
(2) Deng, L.; Chan, H.-S.; Xie, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 2128−2131.
(3) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5219−5230.
(4) McIntosh, R. D.; Ellis, D.; Rosair, G. M.; Welch, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4313−4316.
(5) Deng, L.; Zhang, J.; Chan, H.-S.; Xie, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 4309−4313.
(6) (a) Zi, G.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2001**, 1110−1111. (b) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3836−3838.
(7) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 5415−5427.
(8) Deng, L.; Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 6244−6249.
(9) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097−1105.
(10) See the Supporting Information for details.
(11) For C−Si bond cleavage on silica gel, see: (a) Matsumoto, K.; Uchida, T.; Ikemi, Y.; Tanaka, T.; Asahi, M.; Kato, T.; Konishi, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3645−3653. (b) Lebedev, A. V. *Zh. Obshch. Khim.* **1993**, *63*, 1914.
(12) This transformation can be rationalized via diamond-square-diamond (dsd) process; see: Lipscomb, W. *Science* **1966**, *153*, 373−378.
(13) (a) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128−1133. (b) Hoffmann, R.; Lipscomb, W. N. *Inorg. Chem.* **1963**, *2*, 231−232.
(14) Smith, H. D.; Knowles, T. A.; Schroeder, H. *Inorg. Chem.* **1965**, *4*, 107−111.
(15) Thermal rearrangement of the cage carbons was reported; see: Dustin, D. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 3462−3467.

JA067129E