

Stereocontrol

Deutsche Ausgabe: DOI: 10.1002/ange.201500824 Internationale Ausgabe: DOI: 10.1002/anie.201500824

Unique Stereocontrol in Carborane Chemistry: Skeletal Alkylcarbonation (SAC) versus Exoskeletal Alkylmethylation (EAM) Reactions**

Mario Bakardjiev, Josef Holub, Jan Macháček, Drahomír Hnyk, Bohumil Štíbr,* Zdeňka Růžičková, and Aleš Růžička

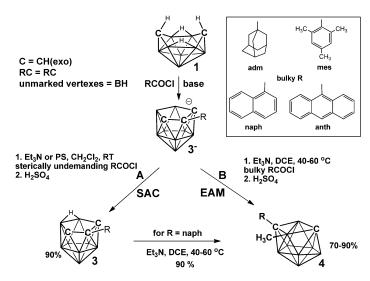
Abstract: Reactions between the arachno-6,9- $C_2B_8H_{14}$ (1) dicarbaborane and acyl chlorides, RCOCl (2), are subject to stereocontrol that completely changes the nature of the reaction products. While most chlorides produce the 8-R-nido-7,8,9- $C_3B_8H_{11}$ (3) tricarbollides (by skeletal alkylcarbonation = SAC), bulky RCOCls (2; where R = 1-adamantyl, 2a; 1-mesityl, 2b; 9-anthranyl, 2c; 1-naphthyl, 2d) in 1,2-dichloroethane (DCE) in the presence of triethylamine at 40-60°C gave a series of entirely different 1-R-2-CH₃-closo-1,6-C₂B₈H₈ (4) dicarbaboranes upon acidification with conc. H₂SO₄ (by $exosleletal\ alkylmehylation = EAM$). Both types of reactions seem to proceed via a common [8-R-nido-7,8,9- $C_3B_8H_{10}$]⁻ (3⁻) anion which in the EAM case is unstable because of steric crowd and undergoes rearrangement via the isomeric $[R-nido-7,8,10-C_3B_8H_{10}]^-$ tricarbollide structures which, on protonation, undergo reductive extraction of one CH vertex to generate the 2-CH₃ substituent in structure 4.

Recently, we have demonstrated that reactions of the [arachno-6,9-C₂B₈H₁₃]⁻ ($\mathbf{1}^-$) anion and various acyl chlorides, RCOCl ($\mathbf{2}$), in the presence of tert-amine bases (Et₃N^[1] or proton sponge^[2]) in CH₂Cl₂, followed by in situ acidification of the anion $\mathbf{3}^-$ thus formed with conc. H₂SO₄, generate a series of neutral alkyl and aryl tricarbollides (11-vertex nido tricarbaboranes)^[3] 8-R-nido-7,8,9-C₃B₈H₁₁ ($\mathbf{3}$) (where R = linear alkyl and simple aryl groups, see also pathway A of Scheme 1). These so-called skeletal alkylcarbonation (SAC) reactions are consistent with an aldol-type condensation between the RCO group and openface hydrogen atoms on the dicarbaborane $\mathbf{1}$,^[2] which is associated with the insertion of the RC unit into the structure

[*] Dr. M. Bakardjiev, Dr. J. Holub, Dr. J. Macháček, Dr. D. Hnyk, Prof. Dr. B. Štíbr Institute of Inorganic Chemistry Academy of Sciences of the Czech Republic Husinec-řež 1001 (Czech Republic) E-mail: stibr@iic.cas.cz Dr. Z. Růžičková, Prof. Dr. A. Růžička Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice Studentská 573, 532 10 Pardubice (Czech Republic)

[**] The work was supported by the Grant Agency of the Czech Republic (project no. P207/11/0705)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500824.



Scheme 1. Stereocontrol in COCI reactions. Most chlorides (path A, SAC reactions) produce tricarbollides 8-R-nido-7,8,9-C₃B₈H₁₁ (3) while bulky chlorides (path B) induce cage rearrangement with resulting alkylmethylation (EAM) to form the disubstituted 1-R-2-CH₃-closo-1,6-C₂B₈H₈ (4) compounds.

of 1^- under elimination of three extra hydrogen atoms as ${\rm H_2O}$ and HCl. The reactions thus result in an effective R-tricarbaborane cross-coupling. However, just recently we have found that reaction in Equation (1) surprisingly proceeds in an entirely different manner when acyl chlorides with bulky (sterically demanding) R-substituents are used as reaction components. Initial results of this study are presented herein.

$$arachno$$
-[6,9-C₂BeH₁₃]⁻ + RCOCl + base → (1)

1 2

 $nido$ - [8-R-7,8,9-C₃BeH₁₀]⁻ + base.HCl + H₂O

3 ↓ H*

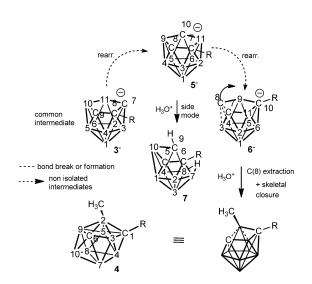
 $nido$ -8-R-7,8,9-C₃BeH₁₁

Scheme 1 (pathway B) shows that treatment of the arachno-6,9- $C_2B_8H_{14}$ (1) dicarbaborane with bulky acyl chlorides, RCOCl (2) (where R=1-adamantyl=adm, 2a; 1-mesityl=mes, 2b; 9-anthranyl=anth, 2c; 1-naphthyl=naph, 2d) in 1,2-dichloroethane (DCE) in the presence of triethylamine (deprotonation agent generating in situ the 1^-



anion) at 40-60 °C gave a series of $1-R-2-CH_3$ -closo-1,6- $C_2B_8H_8$ (4) derivatives (where R = adm, 4a; mes, 4b; anth, 4c, and naph, 4d) as the main products (yield 60-70 %).

As suggested in Scheme 2, it reasonable to suppose that compounds of type 4 are also formed via common intermedi-



Scheme 2. Proposed rearrangement pathways for the formation of 1-R-2-CH₃-closo-1,6-C₂B₈H₈ (4) dicarbaboranes in reactions with bulky acyl chlorides.

ate anions [8-R-7,8,9-nido- $C_3B_8H_{10}$]⁻ ($\mathbf{3}^-$), as documented by the straightforward conversion of the naph anion $\mathbf{3d}^-$ into the neutral compound $\mathbf{4d}$ on protonation under conditions of reaction B (anion $\mathbf{3d}^-$ was isolated under slightly milder conditions and structurally characterized by X-ray diffraction). [1,2] However, anions $\mathbf{3}$ with bulky R groups are evidently unstable owing to the extreme steric crowding between the R-group and terminal cluster hydrogen atoms, which clearly triggers rearrangement to the isomeric tricarbollide anions [8-R-nido-7,8,10- $C_3B_8H_{10}$]⁻ ($\mathbf{5}^-$)[4] and [10-R-nido-7,8,10- $C_3B_8H_{10}$]⁻ ($\mathbf{6}^-$; Scheme 2). The still persisting steric tension is then completely released upon protonation of $\mathbf{6}^-$ with H_2SO_4 [Eq. (2)].

[10-R-
$$nido$$
-7,8,10-C₃B₈H₁₀]⁻ + H⁺ \rightarrow 1-R-2-CH₃- $closo$ -1,6-C₂B₈H₈ (2)
6 4

The protonation clearly results in the attachment of two hydrogen atoms (one from the acid and the other from B(9)H) to the original C(8) vertex. This vertex is then extracted from the cage position to the exohedral site, ^[5] giving rise to the 2-CH₃ substituent under simultaneous breaking of all B–C connections to C(8), except for C(8)–B(9). This process is accompanied by skeletal closure (dotted lines in Scheme 2), which leads unambiguously to the ten-vertex *closo* arrangement **4** with *meta* positioned carbon vertexes without any significant movements within the cage. No migration of the substituted C-vertex to lower-belt positions, as observed in the protonation of the [7-Me-*nido*-7,8,10-C₃B₈H₁₀]⁻ anion

to give 2-Me-nido-2,7,9-C₃B₈H₁₁, [4c] has been detected in this case, evidently due to steric reasons.

It should be noted that neither anions $\mathbf{5}^-$ nor $\mathbf{6}^-$ have been directly isolated in reactions with $\mathbf{2a-2d}$, though isolation of two side products in reaction in Equation (2) (<5% yield), identified as 6-R- arachno-5,6,9- $C_3B_7H_{12}$ (7)^[6] (for R=mes, 7b and anth 7c), clearly points to participation of anion $\mathbf{5}^-$ in the reaction sequence, from which compounds of type 7 arise after hydrolytic removal of the open-face B(11) vertex on protonation (Scheme 2, side mode). [4a]

To further examine the stereocontrol for some aliphatic acyl chlorides, reactions with tBuCOCl (2e), and $n\text{-}C_{11}\text{H}_{23}\text{COCl}$ (2f; lauroyl chloride) were performed under the same conditions. As a result, no compounds of structure 4 were isolated, because of insufficient steric hindrance at C(8) in the 3⁻ stage. Products isolated from these "aliphatic reactions" were the usual^[1,2] compounds of type 8-R-7,8,9- $nido\text{-}C_3B_8H_{11}$ (3; ffor R = tBu 3e and $n\text{-}C_{11}H_{23}$ 3f, Scheme 1, path A, yields $\approx 70\,\%$).

The 1-R-2-CH₃-closo-1,6-C₂B₈H₈ (**4**) dicarbaboranes are chiral disubstituted derivatives of the parent closo-1,6-C₂B₈H₁₀ dicarbaborane (**8**)^[7] with the CH₃ substituent residing between the cage CH(1) and CH(6) vertexes and with the C(1) apex bearing the bulky R group. Figure 1 shows graphi-

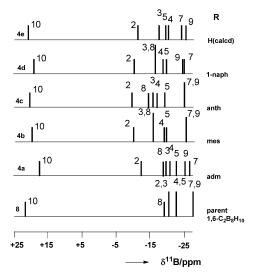


Figure 1. Graphical representation of the ^{11}B NMR chemical shifts and assignments for the parent closo-1,6-C₂B₈H₁₀ (8) and its 1-R-2-CH₃-substituted derivatives (4) revealing the same cluster constitution.

cally the ¹¹B NMR spectra of the substituted dicarbaboranes **4** with that of the parent **8** to reveal straightforward NMR similarities in the ten-vertex *closo*-1,6-dicarbaborane series (for numerical values of NMR shifts see Supporting Information). Owing to the absence of symmetry, individual derivatives **4** show seven BH doublets and one singlet assigned to the substituted B(2) vertex; assignments of individual BH positions were made on the basis of [¹¹B-¹¹B]-COSY measurements.^[8] Typical is the high-frequency resonance assigned to the apical BH(10) boron atom.^[7] The structure of 2-Me*closo*-1,6-C₂B₈H₉ (**4e**) was geometry optimized at the MP2/6-



 $31G^*$ level (see Figure S4 in the Supporting Information) and the found ^{11}B NMR shifts well correlate with GIAO-calculated values for this simplest model for compounds **4** (R = H, see Table S1). Moreover, the structure of 1-adm-2-CH₃-closo-1,6-C₂B₈H₈ (**4a**) was established by an X-ray diffraction study (Figure 2 and Supporting Information), which unambiguously

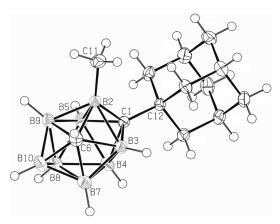


Figure 2. ORTEP representation of the molecular structure of 1-adm-2-CH₃-closo-1,6-C₂B₈H₈ (4a). Selected bond lengths [Å]: C1–C12 1.536(3), C1–B3 1.615(3), C1–B5 1.617(3), C1–B2 1.618(3), C6–B2 1.763(3), C6–B7 1.770(3), B9–B10 1.678(4), B9–B5 1.755(3), B2–C11 1.572(3); angles [°]: C12-C1-B3 127.16(17), C12-C1-B5 126.54(16), B3-C1-B5 106.20(16), C12-C1-B2 127.32(17), B3-C1-B2 70.42(14), B10-C6-B3 116.89(18), B9-C6-B2 61.24(13), B10-C6-B7 59.30(15), B10-B9-C6 57.61(13), B10-B9-B5 114.9(2), B10-B9-B2 114.80(17), B5-B9-B8 61.35(14), B2-B9-B8 106.29(17).

confirms constitution proposed for compounds **4**. The ¹H and ¹³C NMR spectra of the substituted derivatives **4** show resonances attributable to R and one integrating to one CH(6) proton signal along with an upfield resonance of the B-CH₃ methyl group. As shown on **4b** (Supporting Information), neither the ¹H nor the ¹¹B NMR spectrum is temperature dependent within a temperature range -90-+23 °C, which excludes fluxionality of compounds **4**.

It can be concluded that reactions between carborane 1 and acyl chlorides are uniquely stereocontrolled. While sterically undemanding chlorides give tricarbollides 8-R-nido- $7.8.9 - C_3 B_8 H_{11}$ (3; skeletal alkylcarbonation = SAC products),^[1,2] bulky chlorides produce entirely different 1-R-2-CH₃-closo-1,6-C₂B₈H₈ (4) dicarbaboranes (exoskeletal alkylmethylation = EAM reactions). As far as we are aware, [3] this is a lone example of stereocontrol leading to entirely different products in the whole area of boron-cluster chemistry. The formation of compounds 4 is clearly facilitated by the ability of the $[8-R-nido-7,8,9-C_3B_8H_{10}]^-$ (3⁻) cage to isomerize giving, through steric crowding, the isomeric 7,8,10-tricarbollide anions. Compounds 4 are formed from these anions by protonation upon extraction of one CH unit from the C₃B₈ cage to an exoskeletal CH₃ position.^[5] Compounds 4 are the first reliably characterized B-substituted derivatives of closo-1,6-C₂B₈H₁₀ which, moreover, contain quite unusual, bulky substituents bound to the C(1) apex. In progress is further substitution, isomerization, and metal-complex chemistry of these dicarbaboranes.

Experimental Section

4 (R = adm, 4a; mes, 4b; anth, 4c; naph, 4d) and isolation of tricarbaboranes (7; R = mes, 7b; anth, 7c): A solution containing carborane 1 (250 mg, 2 mmol), triethylamine (900 mg, 5 mmol) in 1,2dichloroethane (DCE) (30 mL) was cooled to approximately 0 °C and the corresponding RCOCl chloride (2a-2d; ca. 5 mmol) was then added in small portions under stirring over 0.5 h. The cooling bath was then removed and the stirring continued for 24 h at 40-60 °C. The mixture was then treated with conc. H₂SO₄ (ca. 2 mL, dropwise) under intensive cooling and shaking at ca. 0 °C. The organic layer was carefully separated from the semi-liquid materials sticking on the walls of the reaction flask. The solution thus obtained was then evaporated after adding silica gel (ca. 5 g). The residual material was mounted onto the top of a column packed with silica gel (ca. $2.5 \times$ 20 cm) and then eluted with 100% hexane. The two main fractions of $R_{\rm F}$ (anal.) ca. 0.45–0.50 and ca. 0.25 were collected and evaporated to dryness to isolate typically 1.2-1.4 mmol (60-70%) of compounds 4 from the $R_{\rm F}$ (anal.) ca. 0.45–0.50 fraction and 0.1 and 0.04 mmol (ca. 5 and 2%) of compounds 7b and 7c, respectively from the $R_{\rm F}$ (anal.) 0.25 fraction. Individual derivatives were isolated mostly as semisolid substances. For 4a: m/z (max.) calcd 269.28, found 269.26; elemental analysis calcd (%) for $C_{13}H_{26}B_8$ (M_w 268.83): 58.08 C, 9.75 H; found 57.10 C, 9.35 H. Elemental analysis calcd (%)for $C_{13}H_{23}B_8$ $(M_w 265.81)$: 58.74 C, 8.72 H; found 57.10 C, 8.58 H. For **4b**: m/z(max.) calcd 253.25, found 253.25; elemental analysis calcd (%) for $C_{12}H_{22}B_8$ (M_w 252.79): 57.01 C, 8.77 H; found 56.63 C, 8.54 H. For **4c**: m/z (max.) calcd 311.24, found 311.24; elemental analysis calcd (%) for C₁₇H₂₀B₈ (M_w 310.83): 65.69 C, 6.49 H; found 64.53 C, 6.48 H. For 4d m/z (max.) calcd 261.22, found 261.23; elemental analysis calcd (%) for $C_{13}H_{18}B_8$ (M_w 260.77): 59.88 C, 6.96 H, found 58.91% C, 6.84% H. For **7b** $C_{12}H_{23}B_7$ (M_w 242.99); m/z (max.) calcd 243.25, found 243.25; for **7c** $C_{17}H_{21}B_7$ (M_w 301.03): m/z (max.) calcd 301.23, found 301.23.

3 (R = tBu, 3e; lauroyl chloride, 3 f). The experimental procedure was exactly the same as in the preceding experiment, except that acyl chlorides 2e and 2 f were employed. Collected were chromatographic fractions of $R_{\rm F}$ (anal.) ca. 0.30, from which compounds 3e and 3 f were isolated on evaporation. For 3e: yield 68 %, m.p. 42 °C; m/z (max.) calcd 191.23, found 191.24; Elemental analysis calcd (%) for $C_7H_{20}B_8$ ($M_{\rm w}$ 190.72) calcd 44.08 C 10.57 H; found 43.41 C, 10.24 H. For 3 f: yield 71 %, viscous liquid; m/z (max.) calcd 289.35, found 289.35; Elemental analysis calcd (%) for $C_{14}H_{34}B_8$ ($M_{\rm w}$ 288.91): 58.20 C, 11.86 H, found 57.71 C, 11.54 H.

Conversion of 3d into 4d: A solution of 3d (53 mg, 0.2 mmol) in DCE (20 mL) was treated with Et₃N (1 mL) under heating for 24 h at 40–60 °C. The mixture was then, after treatment with H₂SO₄ as above, worked up by column chromatography as in the first experiment to obtain pure 4d (48 mg, 90%), which was identified by NMR spectroscopy.

See Supporting Information for Tables of NMR data for all compounds, temperature-dependent NMR spectra, ¹H NMR spectra for **4b**, geometry-optimization data for **4e** and crystallography for **4a**.

Keywords: carboranes \cdot dicarbaboranes \cdot NMR spectroscopy \cdot stereocontrol \cdot tricarbaboranes

How to cite: Angew. Chem. Int. Ed. **2015**, 54, 4937–4940 Angew. Chem. **2015**, 127, 5019–5022

5021

^[1] B. Štíbr, M. Bakardjiev, J. Holub, A. Růžička, Z. Padělková, R. Olejník, P. Švec, Chem. Eur. J. 2011, 17, 13156.

^[2] M. Bakardjiev, B. Štíbr, J. Holub, A. Růžička, Z. Padělková, Inorg. Chem. 2013, 52, 9087.

^[3] For a Review see: R. N. Grimes, Carboranes, 2nd ed., Elsevier Science, Amsterdam. 2011.



- [4] For rearrangements of tricarbollide cages see, for example: a) B. Štíbr, J. Holub, I. Císařová, F. Teixidor, C. Viñas, Inorg. Chim. Acta 1996, 245, 129; b) J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Císařová, F. Teixidor, C. Viňas, Z. Plzák, P. v. R. Schleyer, J. Am. Chem. Soc. 1997, 119, 7750; c) A. M. Shedlow, L. G. Sneddon, Collect. Czech. Chem. Commun. 1999, 64, 865; d) B. Štíbr, J. Holub, J. Plešek, T. Jelínek, B. Grüner, F. Teixidor, C. Viñas, J. Organomet. Chem. 1999, 582, 282.
- [5] For extraction of a cage carbon into an exoskeletal position, see: a) G. B. Dunks, M. F. Hawthorne, Inorg. Chem. 1969, 8, 2667; b) J. Plešek, T. Jelinek, B. Štíbr, S. Heřmánek, J. Chem. Soc. Chem. Commun. 1988, 348; c) J. Plešek, B. Štibr, X. L. R. Fontaine, T. Jelinek, M. Thornton-Pett, S. Heřmánek, Inorg. Chem. 1994, 33, 2994; d) B. Štíbr, J. Holub, M. Bakardjiev, Z. Janoušek, Dalton Trans. 2007, 581; e) M. G. S. Londesborough, Z. Janoušek, B. Štibr, I. Císařová, J. Organomet. Chem. 2004, 689, 2702; f) M. G. S. Londesborough, T. Jelínek, B. Grüner, B. Štíbr, I.
- Císařová, M. J. Carr, J. Organomet. Chem. 2005, 690, 2835; g) A. Laromaine, F. Teixidor, C. Viñas, Angew. Chem. Int. Ed. 2005, 44, 2220; Angew. Chem. 2005, 117, 2260; h) M. Finze, Angew. Chem. Int. Ed. 2007, 46, 8880; Angew. Chem. 2007, 119, 9036.
- [6] For other 10-vertex arachno tricarbaboranes see: a) K. Su, B. Barnum, P. J. Carroll, L. G. Sneddon, J. Am. Chem. Soc. 1992, 114, 2730; b) K. Su, P. J. Carrol, G. Sneddon, J. Am. Chem. Soc. 1993, 115, 10004; c) D. E. Kadlecek, D. W. Hong, P. J. Carroll, L. G. Sneddon, Inorg. Chem. 2004, 43, 1933.
- [7] P. M. Garrett, J. C. Smart, M. F. Hawthorne, J. Am. Chem. Soc.
- [8] W. C. Hutton, T. L. Venable, R. N. Grimes, J. Am. Chem. Soc. **1984**, 106, 29.

Received: January 28, 2015 Published online: February 23, 2015

5022