Stereocontrol

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

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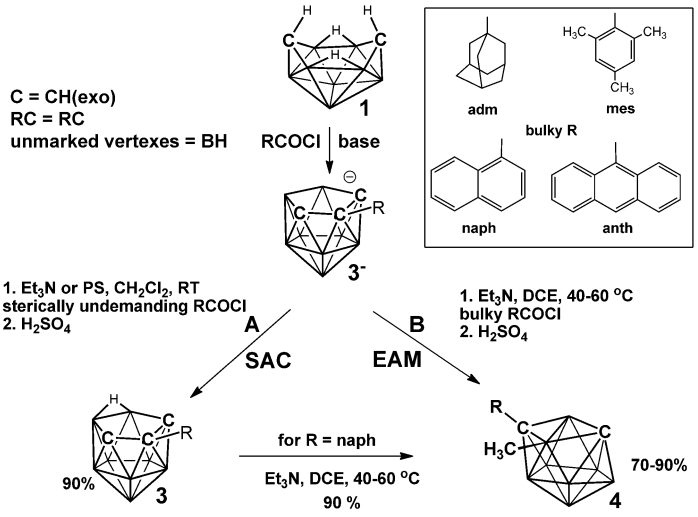
Abstract: *Reactions between the arachno-6,9-$C_2B_8H_{14}$ (**1**) dicarbaborane and acyl chlorides, RCOCl (**2**), are subject to stereocontrol that completely changes the nature of the reaction products. While most chlorides produce the 8-R-nido-7,8,9-$C_3B_8H_{11}$ (**3**) tricarbollides (by skeletal 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-CH_3-closo-1,6-$C_2B_8H_8$ (**4**) dicarbaboranes upon acidification with conc. H_2SO_4 (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-CH_3 substituent in structure **4**.*



Scheme 1. Stereocontrol in COCl reactions. Most chlorides (path A, SAC reactions) produce tricarbollides 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**3**) while bulky chlorides (path B) induce cage rearrangement with resulting alkylmethylation (EAM) to form the disubstituted 1-R-2-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4**) compounds.

Recently, we have demonstrated that reactions of the [*arachno*-6,9-$C_2B_8H_{13}]^-$ (**1**$^-$) anion and various acyl chlorides, RCOCl (**2**), in the presence of *tert*-amine bases (Et_3N[1] or proton sponge[2]) in CH_2Cl_2, followed by in situ acidification of the anion **3**$^-$ thus formed with conc. H_2SO_4, generate a series of neutral alkyl and aryl tricarbollides (11-vertex *nido* tricarbaboranes)[3] 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**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 open-face hydrogen atoms on the dicarbaborane **1**,[2] which is associated with the insertion of the RC unit into the structure of **1**$^-$ under elimination of three extra hydrogen atoms as 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-$C_2B_8H_{13}]^-$ (**1**$^-$) + RCOCl (**2**) + base → *nido*-[8-R-7,8,9-$C_3B_8H_{10}]^-$ (**3**$^-$) + base.HCl + H_2O (1)

↓ H^+

nido-8-R-7,8,9-$C_3B_8H_{11}$ (**3**)

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**$^-$

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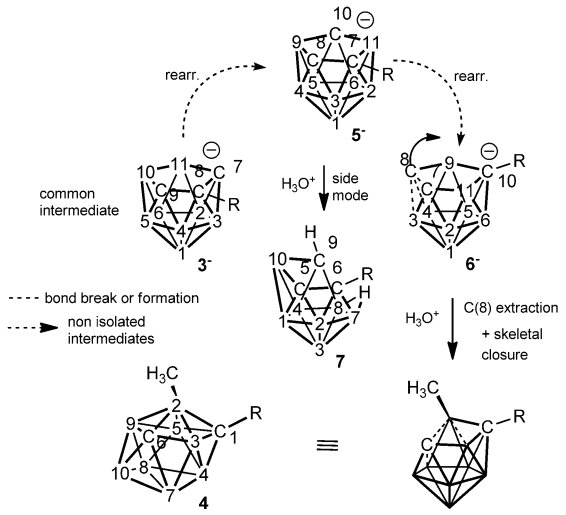
anion) at 40–60 °C gave a series of 1-R-2-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4**) derivatives (where R = adm, **4a**; mes, **4b**; anth, **4c**, and naph, **4d**) as the main products (yield 60–70 %).

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-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4**) dicarbaboranes in reactions with bulky acyl chlorides.

ate anions [8-R-7,8,9-*nido*-$C_3B_8H_{10}]^-$ (**3**$^-$), as documented by the straightforward conversion of the naph anion **3d**$^-$ into the neutral compound **4d** on protonation under conditions of reaction B (anion **3d**$^-$ was isolated under slightly milder conditions and structurally characterized by X-ray diffraction).[1,2] However, anions **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-$C_3B_8H_{10}]^-$ (**5**$^-$)[4] and [10-R-*nido*-7,8,10-$C_3B_8H_{10}]^-$ (**6**$^-$; Scheme 2). The still persisting steric tension is then completely released upon protonation of **6**$^-$ with H_2SO_4 [Eq. (2)].

$$\underset{\mathbf{6}^-}{[10\text{-R-}nido\text{-}7,8,10\text{-}C_3B_8H_{10}]^-} + H^+ \rightarrow \underset{\mathbf{4}}{1\text{-R-2-}CH_3\text{-}closo\text{-}1,6\text{-}C_2B_8H_8} \qquad (2)$$

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-CH_3 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-$C_3B_8H_{10}]^-$ anion to give 2-Me-*nido*-2,7,9-$C_3B_8H_{11}$,[4c] has been detected in this case, evidently due to steric reasons.

It should be noted that neither anions **5**$^-$ nor **6**$^-$ have been directly isolated in reactions with **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 **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 *t*BuCOCl (**2e**), and *n*-$C_{11}H_{23}$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*-$C_3B_8H_{11}$ (**3**; ffor R = *t*Bu **3e** and *n*-$C_{11}H_{23}$ **3f**, Scheme 1, path A, yields ≈ 70 %).

The 1-R-2-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4**) dicarbaboranes are chiral disubstituted derivatives of the parent *closo*-1,6-$C_2B_8H_{10}$ dicarbaborane (**8**)[7] with the CH_3 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-

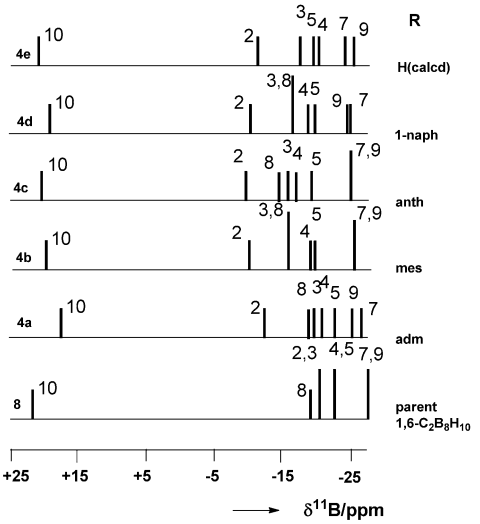


Figure 1. Graphical representation of the ^{11}B NMR chemical shifts and assignments for the parent *closo*-1,6-$C_2B_8H_{10}$ (**8**) and its 1-R-2-CH_3-substituted derivatives (**4**) revealing the same cluster constitution.

cally the ^{11}B 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 [^{11}B–^{11}B]-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-$C_2B_8H_9$ (**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-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4a**) was established by an X-ray diffraction study (Figure 2 and Supporting Information), which unambiguously

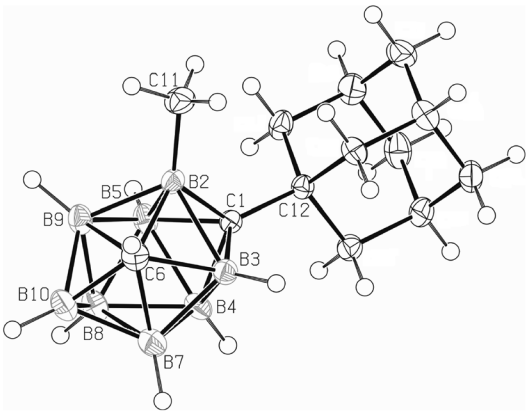


Figure 2. ORTEP representation of the molecular structure of 1-adm-2-CH_3-*closo*-1,6-$C_2B_8H_8$ (**4a**). Selected bond lengths [Å]: C1–C12 1.536(3), C1–B3 1.615(3), C1–B5 1.617(3), C1–B2 1.618(3), C6–B2 1.763(3), C6–B7 1.770(3), B9–B10 1.678(4), B9–B5 1.755(3), B2–C11 1.572(3); angles [°]: C12-C1-B3 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 ^{1}H and ^{13}C 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-CH_3 methyl group. As shown on **4b** (Supporting Information), neither the ^{1}H nor the ^{11}B 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-$C_3B_8H_{11}$ (**3**; skeletal alkylcarbonation = SAC products),[1,2] bulky chlorides produce entirely different 1-R-2-CH_3-*closo*-1,6-$C_2B_8H_8$ (**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 C_3B_8 cage to an exoskeletal CH_3 position.[5] Compounds **4** are the first reliably characterized B-substituted derivatives of *closo*-1,6-$C_2B_8H_{10}$ 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 1,2-dichloroethane (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. H_2SO_4 (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 × 20 cm) and then eluted with 100 % hexane. The two main fractions of R_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_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_F (anal.) 0.25 fraction. Individual derivatives were isolated mostly as semi-solid 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 $C_{17}H_{20}B_8$ (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 = *t*Bu, **3e**; lauroyl chloride, **3f**). The experimental procedure was exactly the same as in the preceding experiment, except that acyl chlorides **2e** and **2f** were employed. Collected were chromatographic fractions of R_F (anal.) ca. 0.30, from which compounds **3e** and **3f** 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_w 190.72) calcd 44.08 C 10.57 H; found 43.41 C, 10.24 H. For **3f**: yield 71 %, viscous liquid; *m*/*z* (max.) calcd 289.35, found 289.35; Elemental analysis calcd (%) for $C_{14}H_{34}B_8$ (M_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 Et_3N (1 mL) under heating for 24 h at 40–60 °C. The mixture was then, after treatment with H_2SO_4 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, ^{1}H NMR spectra for **4b**, geometry-optimization data for **4e** and crystallography for **4a**.

Keywords: carboranes · dicarbaboranes · NMR spectroscopy · stereocontrol · tricarbaboranes

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