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Skeletal Alkylcarbonation (SAC) Reactions as a Simple Design for Cluster–Carbon Insertion and Cross-Coupling: High-Yield Access to Substituted Tricarbollides from 6,9-Dicarba-*arachno*-decaborane(14)

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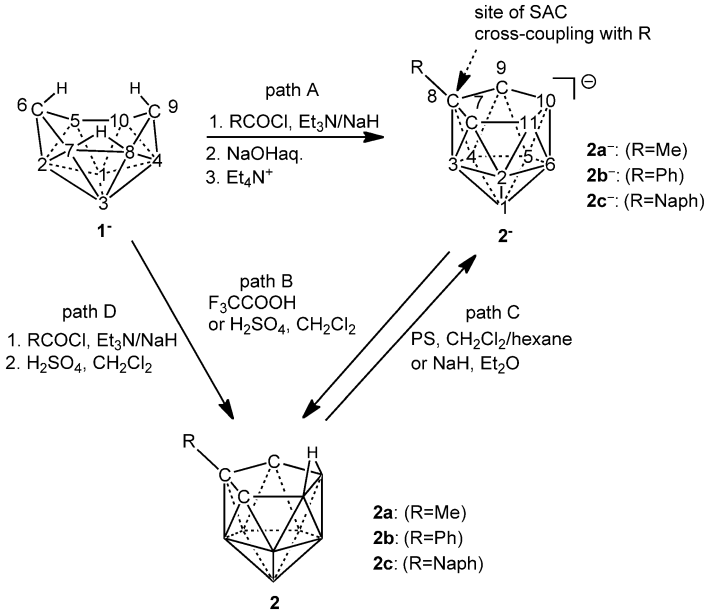
The works by Brellochs and others[1] on degradative insertion of the aldehyde carbon into the structure of the [6-HO-*arachno*-$B_{10}H_{13}$]$^{2-}$ dianion and some metal–carbonyl C-insertion reactions[2] suggested that C=O carbon incorporation procedures might be, in principle, applicable to other cluster systems. To show that this synthetic approach is indeed viable, we report, herein, our preliminary results on a simple and convenient synthesis of the carbon-substituted eleven-vertex *nido* tricarbaboranes (tricarbollides). The reactions are characterized by net inclusion of the C–R vertex into the cluster of *arachno*-6,9-$C_2B_8H_{14}$ through the acyl chloride C=O group, which results in an effective cross-coupling between R and the tricarbollide cage.

Scheme 1 (path A) shows that reactions involving the *arachno*-6,9-$C_2B_8H_{14}$ (**1**) dicarbaborane,[3] two equivalents of Et_3N (in situ generator of [*arachno*-6,9-$C_2B_8H_{13}$]$^-$ (**1**$^-$) and HCl scavenger), NaH (H_2O scavenger), and acyl chlorides RCOCl (exemplified by R = Me, Ph, and Naph (1-Naphthyl)), followed by treatment with aqueous NaOH, and precipitation with R_4NCl (R = Me or Et) led to the isolation of a series of the monoanionic [8-R-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ compounds (**2**$^-$) (**2a**$^-$: R = Me; **2b**$^-$: R = Ph; **2c**$^-$: R = Naph), which were isolated in yields up to 85% (unoptimized, Table 1). The reactions of path A are in accord with the simplified stoichiometry of Equation (1), comprising the deprotonation of **1** along with Cl^- and H_2O elimination.

$$[\textit{arachno}\text{-}6,9\text{-}C_2B_8H_{13}]^- + RCOCl + Et_3N \rightarrow Et_3NH^+[8\text{-}R\text{-}\textit{nido}\text{-}7,8,9\text{-}C_3B_8H_{10}]^- + Cl^- + H_2O \quad (1)$$

As inferred from Scheme 1, the skeletal alkylcarbonation (SAC) reactions are consistent with a regiospecific net insertion of the three-electron carbyne RC≡ unit into the *endo*-skeletal area of **1**$^-$, identified by B5, C6, C9, and B10 vertexes under elimination of three extra hydrogen atoms, such as H_2O and HCl. As exemplified by the structure of the 1-naphthylated species shown in Figures 1 and 2, the reactions can be, in fact, envisaged as a cross-coupling between R and the cage of **1**$^-$ that leaves the coupling process enriched in one more carbon vertex.



Scheme 1. Tricarbollide compounds from the SAC cross-coupling through incorporation of the RC unit into the structure of *arachno*-6,9-$C_2B_8H_{14}$ (**1**). Exo-hydrogen atoms are omitted for clarity; cluster vertexes other than C stand for BH units.

Table 1. Conditions and yields of selected SAC reactions.

R	Path	Solvent	Condition	*t* [h]	Product	Yield [%]
Me	A	CH_2Cl_2	RT	6	**2a**$^-$	82
Me	D	CH_2Cl_2	RT	6	**2a**	70
Ph	A	CH_2Cl_2	reflux	24	**2b**$^-$	85
Ph	B	CH_2Cl_2	RT	1	**2b**	95
Naph	A	CH_2Cl_2	reflux	24	**2c**$^-$	65
Naph	C	CH_2Cl_2/hexane	RT	1	**2c**$^-$	95
Naph	D	CH_2Cl_2	reflux	24	**2c**	65

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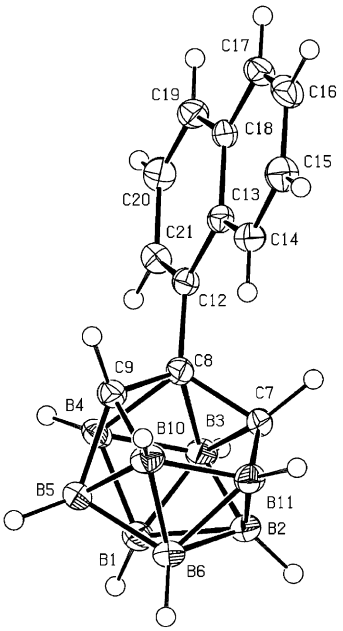

Figure 1. ORTEP representation of the molecular structure of the PSH^+ [8-Naph-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**2c**$^-$) at 50% probability level. The PSH^+ counterion is omitted for clarity. Selected bond lengths [Å] and angles [°]: open face: C7–C8 1.528(3), C7–B11 1.635(4), C8–C9 1.527(3), C9–B10 1.630(4), B10–B11 1.725(4); C8-C7-B11 111.02(18), C7-C8-C9 109.76(19), C8-C9-B10 111.58(19), C7-B11-B10 103.95(19), C9-B10-B11 103.51(19); interbelt distances: mean C–B 1.728(3), mean B–B 1.796(4); lower belt: mean B–B 1.766(4), mean B1–B 1.781(3). The B–H and C–H bond lengths and angles fall within usual limits.

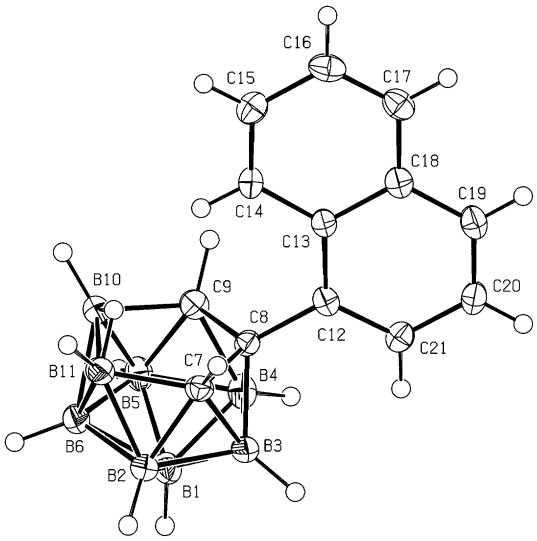

Figure 2. ORTEP representation of the molecular structure of the neutral 8-Naph-*nido*-7,8,9-$C_3B_8H_{11}$ (**2c**) tricarbollide at 50% probability level. Selected bond lengths [Å] and angles [°]: open face: C7–C8 1.531(4), C7–B11 1.656(5), C8–C9 1.533(4), C9–B10 1.668(5), B10–B11 1.850(5); C8-C7-B11 110.1(2), C7-C8-C9 114.3(2), C8-C9-B10 109.7(2), C7-B11-B10 102.8(2), C9-B10-B11 102.4(2); interbelt distances: mean C–B, 1.712(5), mean B–B 1.809(5); lower belt: mean B–B 1.772(5), mean B1–B 1.775(5). The B–H and C–H bond lengths and angles fall within usual limits.

All the [8-R-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**2**$^-$) ions can be protonated by treatment with concentrated H_2SO_4 (or F_3CCOOH) in CH_2Cl_2 to generate a series of neutral compounds with the structure 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**2**) (Scheme 1, path B) in practically quantitative yields; the protonation being consistent with proton addition to the B10–B11 bond in the open face of **2**$^-$. Alternatively, compounds **2** are available directly through pathway D in Scheme 1 by careful treatment with concentrated H_2SO_4 in CH_2Cl_2 while cooling, followed by filtration of the CH_2Cl_2 layer through a silica-gel pad, and removal of the solvent by evaporation. In some cases (R = Naph), products **2** were purified by anaerobic column chromatography on a silica-gel substrate with 20% CH_2Cl_2 in hexane as the mobile phase to isolate fractions of $R_f \approx 0.5$. Deprotonation of compounds **2** (Scheme 1, path C), for example by proton sponge (PS) in CH_2Cl_2/hexane or NaH in Et_2O, leads to anions **2**$^-$, which are much more stable than their neutral counterparts **2**. The structures of the anionic [8-Naph-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**2c**$^-$) and neutral 8-Naph-*nido*-7,8,9-$C_3B_8H_{11}$ (**2c**) compounds were established by X-ray diffraction analyses, which confirmed the C_s-symmetry and 8-substitution on the open face. Also, the structures of all other compounds isolated in this study are in agreement with 8-substitution, as confirmed by ^{11}B, ^1H NMR spectroscopy and MS data (Table 2). The NMR characteristics resemble those reported earlier for the

Table 2. NMR spectroscopy (in CD_3CN) and MS spectrometry data.

Compound	Nucleus	δ [ppm] and assignments	m/z[a]
2a	^{11}B[b]	−0.2 (B2,5), −15.7 (B3,4), −19.9 (B10,11), −28.1 (B6), −33.6 (B1)	149.18/149.17
	^1H[c]	2.93 (2H, H7,9), 1.64 (3H, Me) −2.02 (1H, μ-H10,11)	
2b	^{11}B[b]	−0.3 (B2,5), −16.4 (B3,4), −19.6 (B10,11), −26.6 (B6), −33.3 (B1)	211.19/211.25
	^1H[c]	7.38 (2H, Ph), 7.34 (3H, Ph), 3.29 (2H, H7,9), −1.77 (1H, μ-H10,11)	
	^{13}C[d]	130.0–128.2 (6C, Ph), 47.5 (2C, C7,9), 20.5 (C8)	
2c	^{11}B[b]	1.7 (B2,5), −15.2 (B3,4), −19.2 (B10,11), −25.9 (B6), −33.3 (B1)	260.25/260.21
	^1H[c]	8.01–7.32 (7H, 1-$C_{10}H_7$), 3.23 (2H, H7,9), −1.65 (1H, μ-H10,11)	
	^{13}C[d]	130.9–125.4 (10C, Naph), 49.3 (2C, C7,9), 19.3 (C8)	
2a$^-$[e,f]	^{11}B[b]	−18.0 (BH6/10,11), −19.8 (BH2,5/3,4), −46.3 (BH1)	148.17/148.18
	^1H[c]	−0.25 (3H, Me), 1.27 (2H, H7,9)	
2b$^-$[f,g]	^{11}B[b]	−15.5 (B6), −16.4 (B10,11), −19.6 (B2,5), −20.8 (B3,4), −44.4 (B1)	210.19/210.25
	^1H[c]	−0.19–7.15 (5H, Ph), 1.89 (2H, H7,9)	
2c$^-$[f,h]	^{11}B[b]	−15.8 (B6/10,11), −18.4 (B2,5), −20.2 (B3,4), −45.2 (B1)	260.25/260.21
	^1H[c]	7.80–7.29 (7H, 1-$C_{10}H_7$), 1.62 (2H, H7,9)	

[a] Maximum peaks in the molecular envelope in m/z (calcd/found), measured in the negative mode. [b] $^{11}B\{^1H\}$ NMR data ordered as $\delta(^{11}B)$ in ppm relative to $BF_3{\cdot}OEt_2$ and assignments by [11B–11B]-COSY; all signals are singlets. [c] ^1H NMR data ordered as $\delta(^1H)$ in ppm relative to TMS (intensity, assignment); all signals are singlets. [d] $^{13}C\{^1H\}$ NMR data ordered as $\delta(^{13}C)$ in ppm from TMS (intensity, assignment); all signals are singlets. [e] Me_4N^+ salt. [f] Resonances of the countercation are omitted for clarity. [g] Et_4N^+ salt. [h] PSH^+ salt.

parent *nido* tricarbollides $[7,8,9\text{-}C_3B_8H_{11}]^-$ and 7,8,9-$C_3B_8H_{12}$.[4] The ^{11}B NMR spectra of the C_s-symmetry compounds $\mathbf{2}^-$ consist of 1:2:2:2:1 patterns of doublets, whereas those of the neutral congeners **2** exhibit entirely different 2:2:2:1:1 sets of doublets. The differences being caused by the presence or absence of the open-face bridging μ-10,11 hydrogen.[4] Apart from resonances attributed to the exo-skeletal 8-R substituent, the ^{1}H NMR spectra of compounds $\mathbf{2}^-$ and **2** consist of one intensity 2 singlet (cage CH). As exemplified by the neutral compounds **2b** and **2c**, apart from the low-field resonances due to the aromatic substituents, their $^{13}C\{^1H\}$ NMR spectra expectedly exhibit two broad (^{13}C–^{11}B coupling) 2:1 singlets attributable to the cage C7,9 and C8 carbon vertexes, respectively (a more detailed account on ^{13}C NMR spectroscopy data of other compounds will be given in the full paper). Mass spectra of all compounds are entirely in agreement with the calculated *m/z* values.

The novel SAC method for carbon insertion outlined above brings new dimensions into the so far restricted area of tricarbaboranes[5] since it is extremely flexible and allows for variations in both molecular shape and substituent design. These synthetic tools may be exploited in cluster engineering and B-cage-based biochemistry, for example, by varying substituents on carbon and boron positions in **1** and R in the RCOCl reagent. Other molecular shapes are expected from thermal rearrangement and metal complexation reactions involving the tricarbollide part of the molecule. Moreover, experiments involving bifunctional acyl chlorides and optimization of individual procedures are in progress along with extensive structural investigations. It is also reasonable to expect that the SAC strategy can be applied to cages other than dicarbaborane as well, which may result in substantial extensions and simplifications in the fields of general carborane and heteroborane chemistry.

Experimental Section

Synthesis of the anions $[8\text{-R-}7,8,9\text{-}C_3B_8H_{10}]^-$ (2^-) (Et_4N^+ salts; $2a^-$: R = Me; $2b^-$: R = Ph; $2c^-$: R = Naph), path A: A solution containing carborane **1** (125 mg, 1 mmol), Et_3N (213 mg, 2.1 mmol), CH_2Cl_2 (15 mL), and NaH (48 mg, 2 mmol) was cooled to ≈−40 °C, and the corresponding RCOCl (2.1 mmol) was added in small portions with stirring over 0.5 h. The cooling bath was then removed, and the stirring was continued at RT (for reaction times see Table 1). The solvent was then evaporated, the residue was treated with 5% aqueous NaOH (10 mL) with occasional shaking, and the resulting mixture was then filtered. The filtrate precipitated upon addition of aqueous Et_4NCl (1 M, 1 mL), and the white product was isolated by filtration and dried under vacuum at RT. Individual Et_4N^+ salts can be crystallized from saturated CH_2Cl_2 solutions by careful addition of a hexane layer onto the surface.

Synthesis of neutral $8\text{-R-}7,8,9\text{-}C_3B_8H_{11}$ (2) compounds (2a: R = Me; 2b: R = Ph; 2c: R = Naph), path B: The corresponding Et_4N^+ salts of anions $\mathbf{2}^-$ (reaction scale ca. 0.5 mmol) were carefully treated with CH_2Cl_2 and concentrated H_2SO_4 (≈1 mL) under intensive cooling and shaking at 0 °C. The CH_2Cl_2-soluble components were then separated under N_2 atmosphere on a silica-gel column with 20% CH_2Cl_2 in hexane as the mobile phase to collect fractions of $R_f \approx 0.5$. These were evaporated to give white crystals of compounds **2**, which can be further purified by vacuum sublimation at bath temperatures 100–150 °C. **Path D**: The reaction mixture obtained through path A was, instead of treatment with aqueous NaOH, treated with CH_2Cl_2 and concentrated H_2SO_4 (≈1 mL) under intensive cooling and shaking at 0 °C. Further work-up was the same as that described in path B above. **Path C**: Deprotonation experiments with PS were identical with those reported earlier.[4] Conventional deprotonation of compounds **2** with NaH in dry Et_2O, followed by filtration in vacuo, evaporation of the filtrate, and vacuum drying gave a series of Na^+ salts of anions $\mathbf{2}^-$.

For yields and conditions of individual reactions see Table 1, and NMR and mass spectra are presented in Table 2.

X-ray crystallography: The X-ray data for white crystals of compounds $\mathbf{2b}^-$ and **2c** were obtained at 150 K by using an Oxford Cryostream low-temperature device and a Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[7] The absorption was corrected by integration methods.[8] Structures were solved by direct methods (Sir92)[7] and refined by full matrix least-squares based on F^2 (SHELXL97).[9] Hydrogen atoms could be mostly localized on a difference Fourier map. However, to ensure uniformity of treatment of crystal structures, they were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2\,U_{eq}$ (pivot atom) or of $1.5\,U_{eq}$ for the methyl moieties with C–H = 0.96, 0.97, and 0.93 Å for the methyl and aromatic hydrogen atoms, respectively, and 1.1 Å for B–H and C–H bonds in the carborane cage. Crystallographic data for **2c**: $C_{13}H_{18}B_8$; $M_r = 260.75$; orthorhombic; $P2_12_12_1$; colorless block; $a = 7.1240(3)$, $b = 9.7851(4)$, $c = 21.0540(10)$ Å; $V = 1467.64(11)$ Å^3; $Z = 4$; $T = 150(1)$ K; 13462 total reflections; 2397 independent reflections; $R_{int} = 0.0823$; $R_1 = 0.0659$ (obs. data); $wR_2 = 0.1254$ (all data); GOF = 1.072. Crystallographic data for $\mathbf{2c}^-$: $C_{27}H_{36}B_8N_2$; $M_r = 475.06$; triclinic; *P*-1; light brown block; $a = 9.7450(4)$, $b = 10.2531(5)$, $c = 13.4570(6)$ Å, $\alpha = 90.114(5)$, $\beta = 98.799(4)$, $\gamma = 93.459(4)$°; $V = 1326.24(10)$ Å^3; $Z = 2$; $T = 150(1)$ K; 24727 total reflections; 4146 independent reflections; $R_{int} = 0.0536$; $R_1 = 0.0680$ (obs. data); $wR_2 = 0.1423$ (all data); GOF = 1.081.

CCDC-828706 (**2c**) and CCDC-828705 ($\mathbf{2c}^-$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: acyl chlorides · boranes · carboranes · cross-coupling · synthetic methods

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