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A Practical Synthesis of Isomerically Pure 1,10-Difunctionalized Derivatives of the [*closo*-1-CB₉H₁₀] Anion

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The isomer-free [*closo*-1-CB₉H₈-1-COOH-10-I]⁻ anion (**4**) was prepared in four steps and 10% overall yield from B₁₀H₁₄. The key step is the skeletal isomerization of the [*closo*-2-CB₉H₈-2-COOH-7-I]⁻ anion (**3**) to a mixture of the 10- and 6-iodo derivatives of [*closo*-1-CB₉H₉-1-COOH]⁻ formed in up to a 3:1 ratio. The carboxylic acid **4** was converted to the amine [*closo*-1-CB₉H₈-1-NH₂-10-I]⁻ (**1**) using the Curtius reaction. The relative thermodynamic stability of each product was calculated at the DFT and MP2 levels of theory. The regioselectivity of electrophilic substitution in [*closo*-CB₉H₁₀]⁻ derivatives was briefly investigated using the NBO population analysis of the MP2 wave function.

Introduction

Despite the relatively large number of [*closo*-1-CB₉H₁₀] derivatives prepared to date,[1,2] 1,10-difunctionalized derivatives **I** are still practically unknown. Such derivatives are sought after[3] in the context of the synthesis of linear molecular systems[4,5] and our liquid crystals program in particular.[6,7]

One possible route to such derivatives **I** involves functionalization of the {*closo*-1-CB₉} cage (**II**, Figure 1). While C functionalization proceeds rather smoothly,[8,9] the selective and efficient direct substitution of the B(10) position poses a serious challenge. Previous results showed that electrophilic halogenation of the parent anion, [*closo*-1-CB₉H₁₀]⁻ (**II**, X = H), generally forms the 6 isomer, **III**.[10] The 10 isomer, **I**,
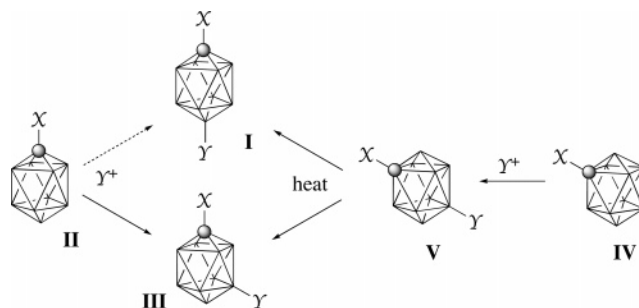

Figure 1. General pathways to disubstituted derivatives of the {*closo*-1-CB₉} cluster.

the expected thermodynamic product, is either absent (iodination and fluorination) or formed as a minor product (<9%). This observed kinetic control of regioselectivity appears to be common for 10-vertex *closo*-boranes.[11–13] In the case of the [*closo*-1-CB₉H₁₀]⁻ anion, the regioselectivity has been ascribed to the higher s-character of the B(10) exoskeletal orbital and consequently higher B–H bond strength as compared with the B(6) position.[10]

The recently discovered[14] Brellochs reaction was exploited[1] in the synthesis of the {*closo*-1-CB₉} derivatives and opened

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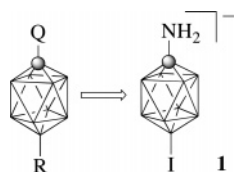(13) Knoth, W. H.; Hertler, W. R.; Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 280–287.

Figure 2. **1** as a precursor to electrically neutral derivatives. Q represents an onium fragment such as sulfonium, pyridinium, or ammonium.

new possibilities in the practical preparation of 1,10-disubstituted derivatives **I**. It was demonstrated that halogenation of [*closo*-2-CB$_9$H$_{10}$] derivatives **IV** occurs selectively at the 7 position.[1] Subsequent thermal rearrangement of the resulting 2,7-disubstituted {*closo*-2-CB$_9$} (**V**) gives a mixture of 10- and 6-substituted {*closo*-1-CB$_9$} in a ≥1:1 ratio.[1]
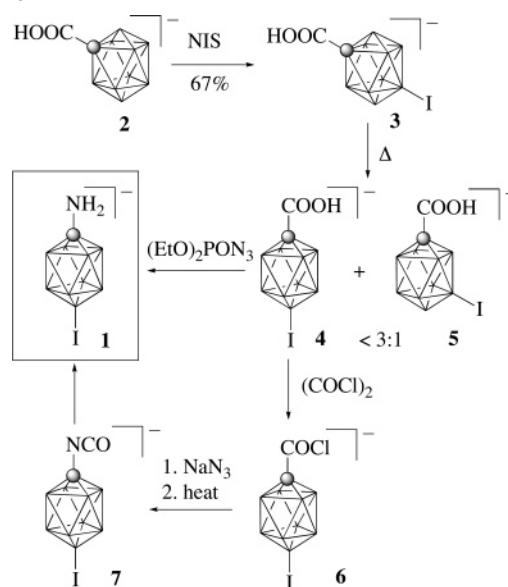
In the context of our interest in electrically neutral, highly polar liquid crystals for electrooptical applications,[6,7] we envisioned 1-amino-10-iodo derivative **1** as a general precursor to this class of materials based on the 10-vertex cluster (Figure 2). The iodine provides a means to introduce alkyl and aryl substituents in Pd-catalyzed coupling reactions reported for {*closo*-1-CB$_9$}[1,9] and other *closo*-boranes.[15] The amino group offers a convenient synthetic handle. It can be transformed to a quinuclidine ring[16,17] or converted into an isolable stable diazo compound.[18] The latter reacted with a range of nucleophiles[18,19] in analogy to arenediazonium salts.

Here we describe a short and practical preparation of isomerically pure **1**. The thermodynamics and regioselectivity of the product formation are discussed with the aid of quantum mechanical calculations.

Results

Synthesis. The preparation of amine **1** starts from the known[20] [*closo*-2-CB$_9$H$_9$-2-COOH]$^-$ anion **2** obtained according to the Brellochs method. The published[20] procedure using 30% excess I$_2$ and stirring for 3 h at ambient temperature gave only about 45% yield of crude **2**, while with 90% excess I$_2$ and 6 h of reaction time, the yield was increased to over 60%. In both cases, the anion **2** was obtained in about 70% purity, with the main contaminant associated with a singlet at 7.0 ppm and a doublet at −10.9 ppm in the ^{11}B NMR spectrum.[21] The crude product also contained up to 10% of the [*closo*-1-CB$_9$H$_9$-1-COOH]$^-$ anion. Iodination of crude **2[NEt$_4$]** with excess *N*-iodosuc-

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(21) This unidentified impurity does not interfere with the preparation of [*closo*-1-CB$_9$H$_9$-1-COOH]$^-$, and a complex ^{11}B NMR spectrum of the mixture yields a clean spectrum of the product.[18]

cinimide (NIS) gave the 7-iodo derivative **3** as a component of a mixture of products (Scheme 1). Conducting the iodination of moist **2[NEt$_4$]** at ambient temperature leads to up to 40% rearrangement of the {*closo*-2-CB$_9$} skeleton and the formation of 10- and 6-iodo isomers (**4** and **5**, respectively) in an approximately 1:1 ratio. Because a solution of isolated crude **3[NEt$_4$]** does not show any appreciable rearrangement over a period of 60 h at ambient temperature, the rearrangement observed during the reaction appears to be a chemically induced, rather than a thermally promoted, process. The rearrangement was limited to <15% of the product by careful drying of the starting **2[NEt$_4$]**. During the iodination process, the intensity of the signals at +7.0 and −10.9 ppm was significantly reduced.

Without separation, the mixture of the [NEt$_4$]$^+$ salts was thermolyzed in boiling acetonitrile, and the resulting anions **4** and **5** were isolated as a mixture of their [NMe$_4$]$^+$ salts in an overall yield of about 15−20% based on the starting B$_{10}$H$_{14}$. ^{11}B NMR analysis showed that the 10- and 6-iodo isomers, **4** and **5**, are the sole products formed in a ratio varying from about 3:2 to 3:1. Results of small-scale thermolysis of the same crude salt **3[NEt$_4$]** show that the ratio of **4** to **5** is less favorable at 50 °C (∼2:1) than at 80 °C (∼5:2). The salt **4[NMe$_4$]** was separated by slow fractional crystallization of the mixture from aqueous EtOH. In one instance, a first recrystallization of a crude mixture of salts increased the ratio from about 3:1 to 15:1, and the second crystallization gave >99% pure [*closo*-1-CB$_9$H$_8$-1-COOH-10-I]$^-$[NMe$_4$]$^+$ salt (**4[NMe$_4$]**). The overall yield of the pure isomer was about 30% based on the crude **2[NEt$_4$]** or about 10% based on B$_{10}$H$_{14}$. The combined mother liquors contained the two isomers in an approximately 1:1 ratio and could be used for the isolation of further quantities of **4[NMe$_4$]**.

The separation of the isomers by recrystallization varies from run to run and presumably depends on the amount of solvent used and the rate of EtOH evaporation. For instance,

we observed that fast crystallization gives a much less satisfactory separation.

The transformation of the carboxyl group of anion **4** to an amino group was accomplished using the Curtius reaction.[22] Treatment of a suspension of acid salt **4[NEt₄]** in CH_2Cl_2 with oxalyl chloride gave the acid chloride **6[NEt₄]** as the sole product, fully soluble in CH_2Cl_2. Without purification, the isolated crude chloride was treated with sodium azide in boiling MeCN to give the isocyanate **7**. Upon hydrolysis, the isocyanate formed the amine **1** isolated as the **1[NMe₄]** or **1[NHMe₃]** salt in about 40−60% unoptimized yield. The purity of the amine varies somewhat from run to run and is possibly related to the quality of anhydrous MeCN. In contrast to **4[NEt₄]**, the **4[NMe₄]** salt did not dissolve upon reaction with $(COCl)_2$, and the acid chloride **6[NMe₄]** presumably was not formed.
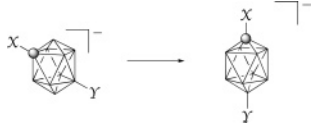
Alternatively, the amine was prepared using a modified Curtius reaction involving phosphoryl azide in the presence of Et_3N.[23,24] Under these conditions, the acid **4[NMe₄]** undergoes deprotonation with NEt_3, as is evident from an about 4 ppm upfield shift of the B(10) signal in the ^{11}B NMR spectrum. Initial attempts using the commercial $(PhO)_2OPN_3$ demonstrated difficulties with the separation of the amine from the phosphoric acid because both are extracted from the acidic solution rather than from alkaline as for a typical organic substrate. Therefore, we used the more hydrophilic $(EtO)_2OPN_3$, which was prepared from the corresponding chloride and NaN_3 in MeCN and used as a crude solution in the reaction with **4[NMe₄]**. The original conditions for the Curtius−Yamada reaction were modified, and the reaction was conducted in dry MeCN in the absence of alcohol. The resulting isocyanate **7** was hydrolyzed during an aqueous workup directly to amine **1**, which was isolated either as oily acid **1[H]** or, more conveniently, as the crystalline salt **1[NMe₄]**. The purity of the product in this method was higher than that obtained in the classical Curtius reaction, and the typical yields were >80%.

Attempts at the conversion of carboxylic acid **4** to the amine **1** using the Schmidt reaction[25] were unsuccessful. Using either classical reaction conditions $(CHCl_3/H_2SO_4)$ and the **4[NBu₄]** salt or **4[H]** in $MeSO_3H$, a complex reaction mixture was obtained that contained a precipitate insoluble in MeCN.

Theoretical Analysis. To better understand the thermodynamics and regioselectivity of the product formation, we conducted quantum mechanical calculations for ground-state structures at the DFT and MP2 levels of theory. Transition structures and their energies were not considered at this point.

Calculations on both levels of theory show that the skeletal rearrangement of the {*closo*-2-CB₉} cluster to the {*closo*-

Table 1. Calculated Exotherms for Skeletal Rearrangement of Selected {*closo*-2-CB₉}⁻ Anions

X	Y	ΔH (kcal/mol)	
		DFT	MP2
H	H	−20.7	−20.7
COOH	H	−22.0	−21.1
H	I	−22.3	−21.8
COOH	I	−23.5	−22.0

1-CB₉} cluster is exothermic by about 22 kcal/mol (Table 1). The exotherm appears to increase slightly with increasing substitution. Thus, introduction of a single substituent increases the exotherm by up to 1.5 kcal/mol for the iodide, while the presence of two substituents (COOH and I) increases the thermodynamic stability of the {*closo*-1-CB₉} isomer by nearly 3 kcal/mol, according to DFT calculations. Calculations at the MP2 level of theory show the same trend, but energy differences are smaller. The calculated energies for the parent anion are consistent with those reported in the literature.[26]

Further analysis shows that the 10-iodo isomers are more thermodynamically stable than the 7- (for the {*closo*-2-CB₉} skeleton) or 6-iodo (for the {*closo*-1-CB₉} skeleton) derivatives by about 1 kcal/mol (Table 2). Again, the difference is smaller by about 0.5 kcal/mol at the MP2 level.

Limited conformational analysis for anions **2** and **3** shows that the structure with the COOH plane approximately orthogonal to the B(1)···B(10) axis (staggered orientation) represents the global minimum. This is consistent with the experimental molecular structure of the former anion,[27] in which the O=C−C−B(1) dihedral angle is about 100° while the calculated angle is 93°. The experimental interatomic distances in **2** are generally overestimated by both methods but are better reproduced by the MP2 method than by DFT calculations.

Calculations for the [*closo*-1-CB₉H₈-1-COOH-6-I]⁻ anion (**5**) revealed that the C_1-symmetric conformer with the B−I bond orthogonal to the COOH plane represents the global minimum (Figure 3). The C_s conformer with the C=O group syn to the I is only slightly higher in energy, while the conformer with the carbonyl group anti to the I is higher by 0.24 kcal/mol than the C_1 form.

Discussion

Preparation of 1,10-disubstituted derivatives of the [*closo*-1-CB₉H₁₀]⁻ anion relies on the regioselectivity of electrophilic substitution at the boron atom. Previous experiments have shown that halogenation gives the 6-halo derivatives as the sole products.[1,10] Bromination[1] and iodination of the {*closo*-2-CB₉} cluster are also kinetically controlled and occur preferentially at the equatorial position. The high

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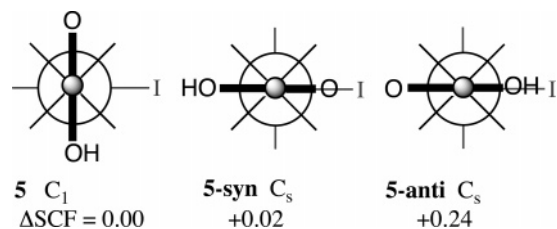(27) Franken, A.; Kilner, C. A.; Kennedy, J. D. *Chem. Commun.* **2004**, 328−329.

Figure 3. Newman projections and relative self-consistent-field energies (kcal/mol) for three conformers of **5**.

Table 2. Difference in Enthalpy of Formation for Selected {closo-CB9} Regioisomers

		$\Delta H = H_B - H_A$ (kcal/mol)			
		DFT		MP2	
isomer A	isomer B				
		X = H	−1.2	X = H	−0.4
		X = COOH	−1.2	X = COOH	−0.4
		X = H	−1.0	X = H	−0.7
		X = COOH	−1.2	X = COOH	−0.8

selectivity for the 7 position in the {closo-2-CB9} cluster is evident from the isolation of [closo-2-CB9H8-7-Br-2-Ph]− in 92% yield.[1] Similarly, high regioselectivity for iodination of [closo-2-CB9H9-2-COOH]− is assumed, but the presence of small quantities of the thermodynamic 10-iodo isomer [closo-2-CB9H8-2-COOH-10-I]− in the reaction mixture cannot be excluded. If it were formed, it would give the undesired 6-substituted [closo-1-CB9H10]− derivative in the rearrangement. Thus, the same kinetic control that prevents the substitution of {closo-1-CB9} at the B(10) position allows the formation of the desired B(10)-substituted product through the {closo-2-CB9} anion.

The origin of the observed kinetic control in iodination of the {closo-CB9} clusters (Table 2) is not clear at the moment, and the preference for equatorial attack cannot be explained satisfactorily by using either charge distribution[28] or hybridization arguments. For instance, NBO analysis of the MP2 wave function for the parent [closo-2-CB9H10]− anion shows a significantly higher negative charge density at the B(10) (−0.23 e) than at the B(7) (−0.18 e) atoms (Figure 4). This charge distribution is little altered by the introduction of the carboxyl group in **2**. Most affected by the substitution is the carbon atom, which becomes less negative by 0.05 e, and the adjacent boron atoms, which become more positive by <0.03 e. However, the same analysis for the parent [closo-1-CB9H10]− anion does show a slightly higher negative charge density at the equatorial position than at the apex. This could provide some rationale for the observed regioselectivity in this cluster, especially that the thermodynamic difference between the two regioisomers is small (Table 2).

Inspection of bonding orbitals shows that in all three anions the B(10) exocyclic orbital has slightly higher
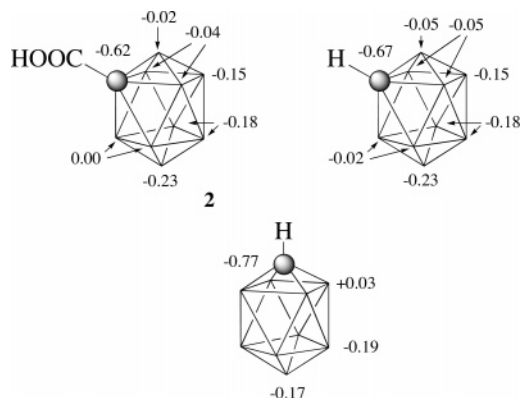
(28) A similar conclusion was reached for the SB9H9 cluster. See refs 11 and 12.

Figure 4. NBO-derived natural atomic charges [MP2/6-31G(d,p) level calculations] in the carboxylic acid anion **2** and parent [closo-CB9H10]− clusters.

s-character (sp2.9) than the equatorial B(6) and B(7) atoms (sp3.0). These differences seem too small to explain the observed regiochemistry of substitution. For comparison, the exocyclic orbital of B(1) in [closo-2-CB9H10]− is sp2.1-hybridized.

The {closo-2-CB9} to {closo-1-CB9} skeletal rearrangement is exothermic and requires relatively low activation energy. This is evident from a facile thermally induced rearrangement, which is usually completed in <24 h at 80 °C. At ambient temperature, such a rearrangement practically does not occur thermally, but apparently it can be chemically induced in the iodination reactions. Thus, in the oxidative ring closure and the preparation of anion **2**, small quantities of the [closo-1-CB9H9-1-COOH]− anion are formed, which presumably undergoes iodination to the 6-iodo isomer **5**. A particularly large degree of rearrangement occurs during iodination of crude and moist **2[NEt4]** with NIS, and the two isomers **4** and **5** are formed in a ∼1:1 ratio. In the end, both processes unfavorably affect the yield of the desired isomer **4** and give rise to the observed variable **4/5** ratio. Thus, limiting the extent of the rearrangement by drying starting **2[NEt4]** and possibly lowering the temperature during the NIS iodination is critical for achieving a high ratio (up to 3:1) for anions **4** and **5**. If the activation energies for the rearrangement of [closo-2-CB9H8-2-COOH-7-I]− and the formation of anions **4** and **5** were proportional to the relative thermodynamic stability of the products, the ratio of **4/5** could be as high as 4:1 at 80 °C, based on MP2 calculations.

The driving force for the rearrangement is the lowering of the coordination number for the more electronegative carbon atom and the simultaneous shift of negative charge density from the boron to the carbon atom. [26] This is illustrated by the charge distribution in the parent clusters [closo-2-CB9H10]− and [closo-1-CB9H10]−. In the rearrangement, the carbon atom gains 0.1 e at the expense of the boron atom (Figure 4).

Summary and Conclusions

The isomerically pure 10-iodo acid [closo-1-CB9H8-1-COOH-10-I]− (**4**) was prepared in four steps from B10H14 in about 10% overall yield. The critical step in the procedure exhibiting the greatest variability is the separation of the

desired **4** from the 6-iodo isomer **5** by recrystallization. The preparation of the mixture of isomeric iodo acids **4** and **5** proceeds without purification of intermediates, and all impurities (up to 30%) are ultimately converted to the products **4** and **5** or are lost in the workup procedures. The two isomers **4** and **5** are formed in a ratio <3:1 in a thermal rearrangement of the {*closo*-2-CB₉} cage, and the overall ratio of the two isomers is controlled by the extent of rearrangement in the NIS iodination step. The current procedure utilizes 4.0 g of $B_{10}H_{14}$, and scaling it up will require optimization of the extraction procedures, especially in the preparation of **2[NEt₄]**.

Iodination and presumably other halogenation reactions of the {*closo*-2-CB₉} and {*closo*-1-CB₉} clusters are kinetically controlled and occur preferentially in the equatorial positions. The apical substituted products are more thermodynamically stable than equatorial isomers by about 1 kcal/mol. Population analysis shows that charge distribution and hybridization of the exocyclic bonding orbitals are not major factors in the regioselectivity of electrophilic substitution in the two {*closo*-2-CB₉} and {*closo*-1-CB₉} clusters.

Computational Details

Quantum mechanical calculations were carried out with the B3LYP[29,30] and MP2(fc) methods using the Linda-Gaussian 98 package[31] on a Beowulf cluster of 16 processors. Calculations involving iodine used the LANL2DZdp effective core potential basis set (available from http://www.emsl.pnl.gov/forms/basisform.html) and 6-31G(d,p) for the remaining elements implemented with the GEN keyword.

Geometry optimizations were undertaken using appropriate symmetry constraints and tight convergence limits. Vibrational frequencies were calculated at the B3LYP/6-31G(d,p) level of theory and were used to characterize the nature of the stationary points and to obtain thermodynamic parameters. Zero-point energy corrections were scaled by 0.9806.[32] Population analysis was obtained using the NBO algorithm[33] supplied in the Gaussian package.

Experimental Section

Solvents were dried and deoxygenated before use, and reagents were used as supplied. Reactions were carried out under dry Ar, and subsequent manipulations were conducted in air. NMR spectra were obtained at 100 MHz (^{13}C), 128.4 MHz (^{11}B), or 400 MHz (^{1}H) in CD₃CN unless otherwise specified. ^{1}H and ^{13}C NMR spectra

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were referenced to the solvent. ^{11}B NMR chemical shifts are relative to the resonance of BF₃·OEt₂ prerecorded in a sealed capillary in CDCl₃ and set to 0.0 ppm.

Preparation of the [*closo*-1-CB₉H₈-1-NH₂-10-I] Anion (1). Method A. Dry salt **4[NEt₄]** (0.80 g, 2.0 mmol) prepared in 80% yield from **4[NMe₄]** was suspended in CH₂Cl₂ (10 mL), and a 2 M solution of (COCl)₂ (2 mL, 4 mmol) was added. The mixture was stirred protected from moisture until all solid dissolved (∼1 h). Volatiles were removed under reduced pressure, and the crude acid chloride **6[NEt₄]** was dried in vacuo [^{11}B NMR δ 22.1 (s, 1B), −14.8 (d, J = 158 Hz, 4B), −20.6 (d, J = 144 Hz, 4B)].

The crude chloride was dissolved in dry MeCN (15 mL), solid NaN₃ (0.20 g, 3 mmol) was added, and the mixture was stirred and refluxed for 3 h. The mixture was cooled, dry CH₂Cl₂ (5 mL) was added, and the mixture was filtered through a glass frit. Solvents were evaporated, and the resulting residue was dried in vacuo, giving a 1:1 mixture of amine **1[NEt₄]** [^{11}B NMR δ 11.5 (1B), −17.9 (4B), −23.3 (4B)] and isocyanate **7[NEt₄]** [^{11}B NMR δ 12.6 (1B), −16.8 (4B), −23.3 (4B)] as the sole products.

The crude product was dissolved in THF (10 mL), 5% HCl (5 mL) was added, and the mixture was stirred at 50 °C for 5 h. Solvents were evaporated, the resulting crude **1[NEt₄]** (∼1.0 g) was treated with 5% HCl (25 mL), and the product was extracted with Et₂O (3 × 50 mL). The combined Et₂O extracts were evaporated, and the product was dried in vacuo to give 0.80 g of [*closo*-1-CB₉H₈-1-NH₃-10-I] (**1[H]**) hydrate as a colorless oil: ^{1}H NMR δ 4.1 (br s); ^{11}B NMR δ (MeCN) 15.0 (s, 1B), −17.5 (d, J = 153 Hz, 4B), −23.0 (d, J = 144 Hz, 4B). The amine was dissolved in water, neutralized with 5% NaOH, and treated with a NHMe₃Cl solution to give 0.66 g of **1[NHMe₃]** as a white solid.

Method B. Crude (EtO)₂OPN₃[34] was prepared from (EtO)₂OPCl (0.76 g, 4.4 mmol, 0.63 mL), which was added dropwise (10 min) to a stirred and gently refluxed mixture of NaN₃ (0.86 g, 13.0 mmol) and dry MeCN (10 mL) under an Ar atmosphere. After 18 h of reflux, the aliquat containing the crude (EtO)₂OPN₃ was decanted from the inorganic salts and via syringe added to a stirred solution of the salt **4[NMe₄]** (0.80 g, 2.2 mmol) in MeCN (3 mL) followed by NEt₃ (4.8 mmol, 0.68 mL). The solution was heated for 18 h under reflux and cooled, an aqueous solution of KOH (2 g in 20 mL) was added, and MeCN was removed under reduced pressure. After the addition of HCl (5%, 200 mL), the mixture was extracted with Et₂O (4 × 50 mL). H₂O (150 mL) was added to the combined Et₂O extracts, and Et₂O was removed under reduced pressure. The aqueous solution was filtered, and HCl (5%, 100 mL) was added to the filtrate. The filtrate was extracted with Et₂O (4 × 50 mL), and 0.80 g of **1[H]** was isolated as in method A.

An aqueous solution of the amine **1[H]** was neutralized with a small excess of 5% NaOH and treated with excess NMe₄Cl. The precipitate was filtered and dried to give 0.58 g (80% yield) of salt **1[NMe₄]**: mp 180−182 °C; ^{1}H NMR δ 2.74 (s); ^{11}B NMR δ 11.8 (s, 1B), −17.8 (d, J = 150 Hz, 4B), −23.3 (d, J = 144 Hz, 4B); IR 3400 (N−H), 2552 and 2520 (B−H) cm^{-1}. Anal. Calcd for C₅H₂₂B₉IN₂: C, 17.96; H, 6.63; N, 8.38. Found: C, 19.01; H, 6.13; N, 7.93.

Preparation of the [*closo*-2-CB₉H₈-2-COOH]⁻ Anion (2). Crude salt **2[NEt₄]** was prepared from B₁₀H₁₄ (4.0 g, mp 104−106 °C) following the literature procedure,[20] with the exception of using 90% excess I₂ and 6 h of reaction time in the oxidation step. The resulting mixture containing ∼70% (by NMR) of the main component was used for the preparation of **3[NEt₄]** without further

(34) Scott, F. L.; Riordan, R.; Morton, P. D. *J. Org. Chem.* **1962**, *27*, 4255–4258.

purification: ^{11}B NMR (**3[NEt₄]**) δ −0.3 (1B), −6.1 (1B), −22.9 (1B), −27.8 (2B), −30.5 (2B), −31.2 (2B) [lit.[20] (acetone-d_6) δ 0.8 (1B), −5.2 (1B), −21.7 (1B), −26.7 (2B), −29.2 (2B), −29.7 (2B)]; additional major signals δ 7.2 (s, 1B), −9.6 (d, 1B), −10.9 (d, 4B), −18.5 (d, 2B), 20.7 (d, 1B); minor signals ([*closo*-1-CB₉H₉-1-COOH]⁻) δ 33.0 (d, 1B), −16.8 (d, 4B), −25.0 (d, 4B) [lit.[20] (acetone-d_6) δ 34.0 (1B), −15.7 (4B), −24.0 (4B)].

Preparation of the [*closo*-1-CB₉H₈-1-COOH-10-I]⁻ Anion (4) and the [*closo*-1-CB₉H₈-1-COOH-6-I]⁻ Anion (5). To a solution of rigorously dried over P₂O₅ crude salt **2[NEt₄]** (3.1 g, 10.5 mmol) in anhydrous CH₃CN (40 mL) was added NIS (3.51 g, 15.6 mmol), and the solution was stirred for 30−48 h at ice bath temperature. After the addition of Na₂SO₃ (0.4 g, 3.2 mmol) followed by HCl (5%, 200 mL), CH₃CN was removed under reduced pressure. The aqueous solution was extracted with Et₂O (3 × 50 mL). Water (150 mL) was added to the combined extracts, and Et₂O was removed under reduced pressure. The aqueous solution was filtered, and [NEt₄]⁺Br⁻ (3.1 g, 15 mmol) was added to the filtrate. After brief stirring, the white microcrystalline precipitate of the [NEt₄]⁺ salt mixture was filtered off, washed with H₂O (50 mL), and dried in vacuo to give 3.0 g (68% yield) of a white solid: ^{11}B NMR (MeCN-d_6) δ (signals characteristic for **3[NEt₄]**) −0.1 (d, J = 162 Hz, 2B), −5.9 (d, J = 164 Hz, 2B), −33.9 (s, 1B).

Without further purification, the mixture of the [NEt₄]⁺ salts (3.0 g, 7.1 mmol) was dissolved in CH₃CN (20 mL) and heated for 20 h under reflux. After cooling, the solvent was removed in vacuo. After the addition of HCl (5%, 100 mL), the mixture was extracted with Et₂O (3 × 50 mL). H₂O (50 mL) was added to the combined Et₂O extracts, and Et₂O was removed under reduced pressure. The aqueous solution was filtered, and [NMe₄]⁺Cl⁻ (1.64 g, 15 mmol)

was added to the filtrate. The resulting white precipitate was filtered off and dried in vacuo to give 2.51 g of a crude mixture of the [NMe₄]⁺ salts of **4** and **5** in a ratio ranging from about 3:2 to 3:1 (by integration of the signals at +18.8 and −29.1 ppm in the ^{11}B NMR spectrum).

The mixture of the [NMe₄]⁺ salts (2.5 g) was dissolved in hot EtOH (80 mL), water (80 mL) was added, and the solution was left to crystallize in a tall Petri dish, yielding 1.90 g of about 92% pure **4[NMe₄]**. One more crystallization gave 1.30 g (11% yield based on B₁₀H₁₄) of >99% pure isomer: mp 244−245 °C; ^{1}H NMR (acetone-d_6) δ 0.5−2.5 (br m, 8H), 3.43 (s, 12H), 10.9 (br s, 1H); ^{11}B NMR δ 18.8 (s, 1B), −16.6 (d, J = 156 Hz, 4B), −21.2 (d, J = 143 Hz, 4B); IR 2570 and 2524 (B−H), 1695 (C=O) cm⁻¹. Anal. Calcd for C₆H₂₁B₉INO₂: C, 19.83; H, 5.82; N, 3.85. Found: C, 20.06; H, 5.76; N, 3.87.

[*closo*-1-CB₉H₈-1-COOH-6-I]⁻[NMe₄]⁺ (5[NMe₄]): ^{11}B NMR (after subtracting signals due to the 1,10-isomer **4[NMe₄]**) δ 31.6 (d, J = 174 Hz, 1B), −14.5 (d, J = 156 Hz, 2B), −15.0 (d, 2B), −22.5 (d, J = 169 Hz, 2B), −25.1 (d, J = 140 Hz, 1B), −29.2 (s, 1B).

Deprotonation of [*closo*-1-CB₉H₈-1-COOH-10-I][NMe₄] with NEt₃. A solution of **4[NMe₄]** (10 mg) in CD₃CN was treated with NEt₃ (2.5 equiv), and an NMR spectrum was recorded: ^{11}B NMR δ 15.1 (s, 1B), −17.4 (d, J = 154 Hz, 4B), −21.5 (d, J = 141 Hz, 4B).