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The preparation of [*closo*-1-CB_9H_8-1-COOH-10-(4-$C_3H_7C_5H_9S$)] as intermediate to polar liquid crystals

Jacek Pecyna [a], Richard P. Denicola [a], Bryan Ringstrand [a], Aleksandra Jankowiak [a], Piotr Kaszynski [a,b,*]

[a] Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States
[b] Faculty of Chemistry, University of Łódź, Tamka 12, 91403 Łódź, Poland

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ABSTRACT

The preparation of iodo acid [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ (**1**) is optimized and scaled from 1 to 40 g of $B_{10}H_{14}$. The improved preparation of the [*arachno*-6-CB_9H_{13}-6-COOH]$^-$ (**5**) uses four times smaller volume and can be run conveniently in up to 40 g scale in a 3-L vessel. The optimized oxidation of **5** to [*closo*-2-CB_9H_9-2-COOH]$^-$ (**4**) requires less oxidant, 12 times smaller volume, and significantly shorter reaction time. The overall yields of the iodo acid **1** as the $[NMe_4]^+$ salt are typically 8–10% (10–12 g) for 40 g of $B_{10}H_{14}$. The iodo acid **1** was transformed to amino acid **8**, then to dinitrogen acid **10**, and finally to sulfonium acid **2[3]** in overall yield of about 13%. The search for a more efficient phosphine ligand for the Pd-catalyzed amination process was not fruitful. Three routes to the sulfonium acid **2[n]** were investigated, and the best yield of about 47% was obtained for Cs_2CO_3-assisted cycloalkylation. Liquid crystalline ester of acid **2**[**3**] and 4-butoxyphenol was prepared and investigated.

1. Introduction

The Brellochs' synthesis [1,2] of the {CB_9} cluster from $B_{10}H_{14}$ followed by Kennedy's halogenation and rearrangement [3] of the {*closo*-2-CB_9} opened up possibilities for preparing 1,10 -difunctional derivatives of the [*closo*-1-CB_9H_{10}]$^-$ anion. Subsequently, we reported [4] the first practical synthesis of isomerically pure iodo acid [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ (**1**), which has been the key intermediate in the synthesis of new classes of polar [5–7] and ionic [8] liquid crystals **I** and **II**, respectively (Fig. 1). In this context, the carboxyl group in **1** has been converted into X = ester [6–9], amino [4,8], dinitrogen [8], azo [8], and sulfonium [5,9] groups, while the iodine to Y = alkyl [5,8], amino [9], dinitrogen [9], pyridinium [6,7,9], and sulfonium [6,9] derivatives. Among the 10-sulfonium derivatives are esters of acid **2**[**5**], such as **3[5]**, which exhibit nematic behavior [6] (Fig. 2). Due in part to their fluxional behavior and facile epimerization at the sulfur center, esters **3[5]** such as the 4-butoxyphenyl ester **3[5]a**, are sufficiently soluble in liquid crystalline hosts and are of interest for display applications. However, further exploration of these unusual molecular materials and their practical applications require significant quantities of the iodo acid **1** and is limited by access to [*closo*-2-CB_9H_9-2-COOH]$^-$ (**4**).

The preparation of *closo* acid **4** (Scheme 1) described by Kennedy involves large volumes of solvents and large excess of reagents [10]. For instance, the total volume of solution in the Brellochs' reaction is 100 mL/g of $B_{10}H_{14}$. The second step, an oxidation, uses an even larger volume of solvents at 150 mL/g of *arachno* acid **5**. Thus, the first two reactions used in the preparation of *closo* acid **4** are impractical to scale up in their present form.

Here we describe optimization of the synthesis of acid **4** and a convenient procedure for its preparation that uses up to 40 g of $B_{10}H_{14}$ at a time, large-scale preparation of iodo acid **1**, and its conversion to sulfonium acid **2**[**3**]. Finally, we demonstrate liquid crystalline ester **3[3]a** derived from acid **2[3]** and compare its properties those of the higher homolog **3[5]a**.

2. Results and discussion

2.1. Optimization of synthesis of [closo-2-CB_9H_9-2-COOH]$^-$ (4)

Initially, we reproduced the original procedure [10,11] for the Brellochs' reaction of $B_{10}H_{14}$ with glyoxylic acid (run 1, Table 1). This reaction conducted at 1 and 4 g scale of $B_{10}H_{14}$ gave consistent results of the *arachno* acid **5** in about 60% yield[1] and 85–90% purity,

* Corresponding author at: Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States.
E-mail address: piotr.kaszynski@vanderbilt.edu (P. Kaszynski).

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[1] The yields of the crude *arachno* acid **5** are not fully reliable. The solid contains boric acid and some other insoluble impurities (upon dissolution in NMR tube with CD_3CN or acetone-d_6), and may also be partially hydrated. Therefore, the most reliable yields are obtained by combining the first two processes: insertion and oxidation (30–40% yield on average).

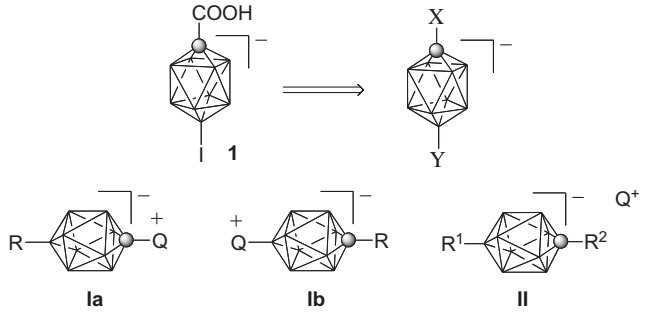


Fig. 1. Acid **1** as a precursor to 1,10-difuctionalized derivatives of the {*closo*-1-CB_9} cluster, which include polar (**I**) and ionic (**II**) liquid crystals. Q^+ is pyridinium, ammonium or sulfonium, R, R^1, R^2 = alkyl, ester. For X and Y see text.

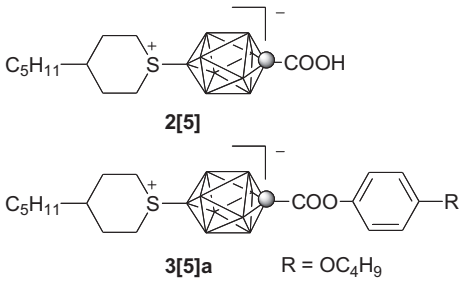
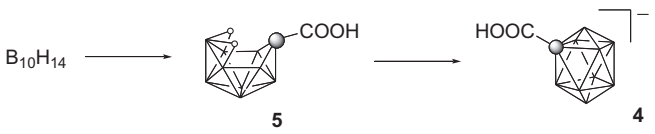


Fig. 2. Structures for acid **2**[**5**] and ester **3**[**5**]**a**.



Scheme 1. Preparation of *arachno* acid **5** and subsequent oxidation to *closo* acid **4** starting from $B_{10}H_{14}$.

which is comparable to 53% originally reported [10,11]. The ^{11}B NMR spectrum was nearly identical to that reported for the *arachno* acid **5** with the main impurity associated with the signals at −12.1 and −0.5 ppm in addition to boric acid at 20.2 ppm in the NMR spectrum.

Since the original procedure uses several-fold excess of glyoxylic acid and base relative to that required by stoichiometry (Eq. (1)), our attempts were directed at reducing amounts of the reagents and the volume of the solution. Optimization reactions were conducted on 1 g of $B_{10}H_{14}$.

$$B_{10}H_{14} + 3OH^- + CHOCOOH \rightarrow [\textit{arachno}\text{-}6\text{-}CB_9H_{13}\text{-}6\text{-}COO^-]^- + B(OH)_4^- + H_2 \quad (1)$$

$$[\textit{arachno}\text{-}6\text{-}CB_9H_{13}\text{-}6\text{-}COO^-]^- + 2I_2 + 5OH^- \rightarrow [\textit{closo}\text{-}2\text{-}CB_9H_9\text{-}2\text{-}COO^-]^- + 4I^- + 5H_2O \quad (2)$$

Reducing the amount of glyoxylic acid by half gave lower yield of the product with comparable purity in a range of 85–95% (run 2). When the amount of base was also reduced by half and less water used (run 3), the product was obtained in higher yield and similar purity. Further reduction of the amount of glyoxylic acid led to unstable product that decomposed upon isolation (run 4). Other experiments showed that the volume of water could be reduced further without affecting the yield or purity (runs 5–7). In all reactions in which the amount of glyoxylic acid was reduced (runs 3, 4, 8, and 9), the precipitation procedure was complicated by excessive foaming during quenching with HCl, and frequent formation of the product as a clumpy, sticky goo rather than a microcrystalline solid. Even though the amount of base can be reduced, excess base helps with fast dissolution of $B_{10}H_{14}$.

Table 1
Optimization of preparation of [*arachno*-6-CB_9H_{13}-6-COOH]$^-$ $[NEt_4]^+$ (**5**).[a]

Run	$B_{10}H_{14}$ (mmol)	KOH (mmol)	HOOCCHO (mmol)	H_2O (mL)	Yield[b] (%)
1	8.2	112.5	55	50	62
2	8.2	112.5	28.2	50	47[c]
3	8.2	70	28.2	35	79[c]
4	8.2	60	12.4	15	[d]
5	8.2	60	28.2	10	62[c]
6	8.2	53.3	20.5	10	72[c]
7	8.2	112.5	55	20	78
8	8.2	70	28.2	15	81[c]
9	8.2	85.7	28.2	10	56[c]
10a	8.2	112.5	55	10	49
Scale up					
10b	82	1120	543	100	67 avr
10c	164	2240	1080	200	70 avr
10d	246	3360	1620	300	61[e]
10e	327	4480	2160	500	66–71

[a] All reactions are run at ice bath temperature; reaction time 2 h.
[b] Product precipitated from the reaction mixture. See footnote 1.
[c] The precipitate often is a tacky goo instead of crystalline solid.
[d] Expected product **5** was not formed; excessive decomposition during workup.
[e] Crushed ice was added to the basic solution. See Section 4.

Considering the difficulties with isolation of the *arachno* acid **5** with smaller amounts of the reagents, we decided to pursue the concentrated version of the original procedure. Thus, decreasing the volume of water by four times gave the *arachno* acid **5** in yield and purity comparable to the original procedure (run 10a versus run 1). Additional reduction of volume of the reaction was accomplished by increasing the concentration of HCl from 5% in the original procedure to 18%. Overall, this procedure reduces the volume of water from 100 to 25 mL/g of $B_{10}H_{14}$ and is considered a significant improvement. This procedure (run 10a) was successfully scaled from 1 to 10 g (run 10b) and then to 20 g (run 10c) of $B_{10}H_{14}$. The 10-g scaled reaction was reproducible over several runs giving average yields of 60% with purities of about 90%.

The 20 g scale reaction posed new challenges related to heat dissipation during acid–base reactions (addition of glyoxylic acid and quenching with HCl) and consequently exotherm control. The reaction was conducted conveniently in a 2-L vessel in an ice-bath with efficient mechanical stirring and an internal thermometer. The reaction was closely reproducible as long as the internal temperature of the mixture was maintained around 5 °C, and gave an average yield of 70% with purities of about 90% over several runs. The total volume of the aqueous solution after quenching with HCl is approximately 500 mL. Insufficient acidification and failure to adjust the pH to about 3 lead to the formation of pyrophoric products, as it was observed in one instance: product of a reaction on a 50 g scale of $B_{10}H_{14}$ spontaneously ignited after overnight drying. ^{11}B NMR spectrum of the pyrophoric material revealed a possibly different chemical structure than that routinely obtained at 20 g with fully adjusted pH.[2]

The preparation of *arachno* acid **5** was successfully scaled to 30 g of $B_{10}H_{14}$ by adding crushed ice to the basic solution and using

[2] The ^{11}B {^1H} NMR spectrum of the unknown pyrophoric product in CD_3CN contained characteristic signals at 9.0, −13.0, −15.5, −18.5, −22.2, −31.2, −35, −39.2 ppm.

less concentrated HCl (12% versus 18%) during work-up for better control of the exotherm (run 10d). Finally, the reaction was scaled to 40 g of $B_{10}H_{14}$ and run reproducibly several times in a 3-L vessel (run 10e). The exotherm of neutralization processes is controlled by using crushed ice (200 g) and freezer-chilled 20% solutions of HCl.

Overall, results indicate that good yields and purity of *arachno* acid **5** can be obtained using fewer equivalents of base and glyoxylic acid in the Brellochs' reaction. However, the workup procedure is complicated by excessive foaming during quenching with HCl, and the sticky, difficult to work with form of the product. This is avoided by using larger amounts of reagents as described in the original procedure. The desired reduction of the volume of the reaction is achieved by using approximately six times more concentrated solution of base and four times more concentrated HCl. These reactions also require finely ground $B_{10}H_{14}$ for quick dissolution at <5 °C and slow addition of glyoxylic acid and HCl to allow for efficient heat dissipation.

The oxidation of the *arachno* acid **5** to *closo* acid **4** was originally conducted using hypoiodite under basic solutions [10,11]. The stoichiometry of the oxidation of the *arachno* acid **4** requires 2 mol of I_2[3] (Eq. (2)), while the original procedure used 2.75 mol of I_2 with a total volume of aqueous solution of 150 mL/g of *arachno* acid **5**. Since excess I_2 is small, our focus was mainly on reducing the volume of solvents used in the process and exploring alternative oxidants.

As we reported earlier [4], a briefly optimized oxidation required up to 90% excess of I_2 at ambient temperature, which was the recommended temperature in the original procedure [10,11]. The same reaction run at ice bath temperature was completed with stoichiometric (2 mol) amounts of I_2 (run 1, Table 2), less base, and in shorter time (1.5 versus 6 h). The volume of water was reduced by a factor of 12 from 150 to 12 mL/g of *arachno* acid **5**. The need for only stoichiometric amounts of I_2 and hence its more efficient use at 0 °C may be explained by the higher stability of hypoiodite at low temperature. The progress of the oxidation was monitored by ^{11}B NMR of a small aliquot of the basic solution in D_2O. The analysis demonstrated that the reaction is completed in less than 2 h instead 6 h as originally reported. To assure complete oxidation of **5**, a 15% excess I_2 was used for large-scale preparations of acid **4**, which was typically obtained in 43–58% yield (run 2, Table 2).

We also tested hypobromite as the oxidant for the *arachno* acid **5**, but the results were significantly less satisfactory (runs 3–6, Table 2). The solutions of the hypobromite had to be prepared separately, required relatively large volumes of the aqueous phase, and the yield was low although with comparable purity.

2.2. Optimization of synthesis of [closo-1-CB_9H_8-1-COOH-10-I]$^-$ (**1**)

The previously reported iodination [4] of *closo* acid **4** with 50% excess NIS to form iodo acid **6** (Scheme 2) was used without modification on a scale of up to 30 g of *closo* acid **4**. The impurities in the *arachno* acid **5** were largely removed during the oxidation step and nearly completely during work-up after iodination. The iodination step now has higher yield of about 90% than the originally reported [4] (67% yield) due to higher purity of acids **5** and **4**.

In addition, two other iodinating reagents, ICl and I_2, were investigated for the preparation of iodo acid **6**. Reactions of *closo* acid **4** with NIS, I_2, and ICl were conducted at the 100 mg scale for 72 h at −10 °C. Reaction with NIS reproduced the results previously obtained on a large scale, I_2 gave only recovered starting material **4**, and ICl gave iodo acid **6** with only 20% conversion.

The final two steps, rearrangement of the iodo acid **6** to a mixture of iodo acids **1** and **7** (Scheme 2) followed by separation of isomers, remain straightforward, and scaling up was simple. Starting from a 38 g batch of iodo acid **6**, thermal rearrangement gave an expected [4] 3:2 mixture of iodo acids **1** and **7** (68–86%), which after two recrystallizations from aqueous EtOH gave about 11 g of 99% pure isomer **1**. Attempts to harvest more iodo acid **1** from the remaining mixture of the isomeric iodo acids were unsuccessful.

Table 2
Optimization of formation of [*closo*-2-CB_9H_9-2-COOH]$^-$ $[NEt_4]^+$ (**4**).[a]

Run	**5** (mmol)	KOH (mmol)	Oxidant	(mmol)	H_2O (mL)	Time (h)	Yield (%)
1	5	40	I_2	10	15	0.5	54
2	217	1742	I_2	500	645	2	43–58
3	5	40	Br_2	15	15	0.5	35
4	24.3	192	Br_2	97.2	72.3	0.75	23
5	62	496	Br_2	248	92	0.75	34[b]
6	20.8	166	Br_2	83.2	62.4	0.75	[c]

[a] All reactions are run at ice bath temperature.
[b] Solution turned black upon addition of HCl.
[c] Resubmission of product from reaction 5 led to decomposition.

2.3. Optimization of synthesis of [closo-1-CB_9H_8-1-COOH-10-NH_3] (***8***)

The originally reported [9] amination of the iodo acid **1** to amino acid **8** (Scheme 3) was accomplished using 2-(dicyclohexylphosphino)biphenyl (**A**) as a ligand for the Pd(0) catalyst. The reaction requires a large excess (>10 equiv.) of LiHMDS and gives significant amounts, up to 20%, of the deiodinated product [*closo*-1-CB_9H_9-1-COOH]$^-$ (**9**). In an effort to improve this process, we investigated six other ligands *L* (Chart 1), which have been used for amination of aromatic halides [12].

Test reactions were run on a 50 mg scale of iodo acid **1** using conditions reported previously [9] and a phosphine ligand *L* selected form the list in Chart 1. After 24 h of reflux and full workup, the reaction mixtures were analyzed as ethereal extracts from aqueous acid. ^{11}B NMR results demonstrated that for ligand **B** the iodo acid **1** was practically consumed and the amino acid **8** was contaminated with about 20% of deiodinated product **9** and the same amounts of 10-phosphonium byproducts. The same reaction run on a 1 g scale gave the amino acid **8** isolated in 44% yield. Conversion of **1** was only 50% when ligand **C** was used, and the reaction mixture contained additional by-products presumably decarboxylation products. No conversion of iodo acid **1** was observed for other ligands, DPPF (**D**), XANTPHOS (**E**), BINAP (**F**), and PEPPSI-IR (**G**).

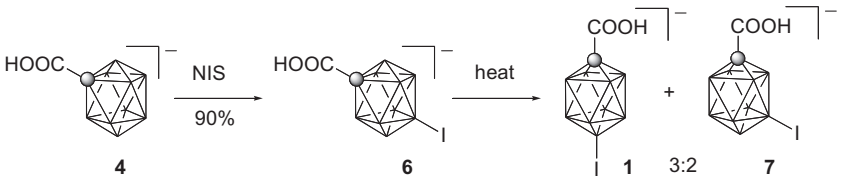
Overall, the amination reaction was conveniently run on a 15 g scale of iodo acid **1** using phosphine **A** as the ligand giving the amino acid **8** in 43–56% yield. It appears that ligands based on the 2-(dicyclohexylphosphino)biphenyl core, such as **A** and **B**, are particularly effective for *B*-amination [9] and *B*-amidation [13] of *closo*-boranes.

2.4. Synthesis of [closo-1-CB_9H_8-1-COOH-10-(4-$C_3H_7C_5H_9S$)] (***2[3]***)

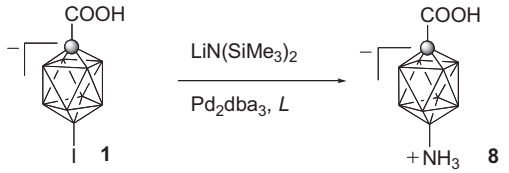
Amino acid **8** was converted to the dinitrogen acid **10** with a typical yield of 55–65% by diazotization with $NO^+BF_4^-$ in pyridine solutions as described before [9] (Scheme 4). Subsequent thermolysis of **10** in Me_2NCHS gave protected mercaptan **11**, which was cycloalkylated with dibromide [14] **12** under hydrolytic conditions to form the sulfonium acid **2[3]**.

The alkylation reaction run under conditions described previously [6] for **2[5]**, $Me_4N^+OH^-\cdot 5H_2O$ in MeCN, gave the acid **2[3]** in a modest yield of about 36% after recrystallization, which is comparable to that obtained [6] for **2[5]**. ^{1}H NMR spectra revealed formation of olefins and esters as by-products. The latter were converted to the acid by hydrolysis with alcoholic NaOH. However, the

[3] The original paper mistakenly shows only 1 mol of I_2 per more of *arachno* acid **5**.



Scheme 2. Transformation of *closo* acid **4** to iodo acid **1**.



Scheme 3. The preparation of amino acid **8**.

formation of the olefin complicated the purification of the acid. In effort to improve the yield and simplify the procedure, we investigated several other conditions and methods for the formation of acid **2**.

Changing the base from $Me_4N^+OH^-\cdot 5H_2O$ to Cs_2CO_3 resulted in improvement of the yield of **2[3]** to 45–47% based on crude protected mercaptan **11** or 42–44% based on dinitrogen acid **10**. Although the carboxyl group was still esterified under these conditions, the olefin formation was not observed. In both methods the crude acid can be purified additionally by converting to methyl ester **3[3]b**, chromatography, and basic hydrolysis back to acid **2[3]**. Using this method we also prepared tetramethylenesulfonium acid **13**, which was isolated as its methyl ester **14** (Scheme 5).

To avoid complications of formation of esters with dibromide **12**, we focused on methyl ester **15** prepared from the reported [9] dinitrogen ester **16** (Scheme 6). Cycloalkylation of **15** with dibromide **12** in the presence of Cs_2CO_3 and catalytic amounts of $Bu_4N^+Br^-$ in MeCN at 60 °C gave acid **2[3]** in 45% yield after hydrolysis of the intermediate methyl ester **3[3]b**. It was apparent that the reaction of the ester was slower than for the acid, and required higher temperatures presumably due to electron withdrawing effect of the COOMe group, when compared to the COO^-, and consequently lower reactivity of the sulfur atom.

Finally, we explored the formation of sulfonium acids **2[n]** directly from dinitrogen derivative **10** and appropriate thiane **17[n]**. Since the dinitrogen acid **10** was insoluble in thiane, we focused on its methyl ester **16** [9]. Thermolysis of the ester in solutions of the parent thiane (**17[0]**) gave the expected sulfonium ester **3[0]b** in 64% yield as the first less polar fraction. The second fraction contained a very polar by-product, presumably product of C–H insertion (Scheme 7), which was identified by the downfield shift of the B(10) nucleus (δ = +48 ppm), characteristic for B(10)-alkyl derivatives [8], and mass spectrometry. A similar reaction of **16** with 4-propylthiane (**17[3]**) gave the ester **3[3]b** in 49% yield. Considering the yield of preparation of ester **16** and the hydrolysis step, the overall efficiency of this method is comparable to that involving cycloalkylation of **11** with dibromide **12** (Scheme 4).

2.5. Liquid crystalline properties of esters

Ester **3[3]a** was prepared by esterification of sulfonium acid **2[3]** with 4-butoxyphenol (Scheme 8). Thermal analysis of **3[3]a** revealed a monotropic nematic phase with the clearing temperature of 96 °C (Table 3). Surprisingly, this temperature for the N–I transition is nearly the same as observed [6] for its higher homolog **3[5]a**. However, the melting temperature is lower by 10 K for **3[3]a** than for **3[5]a**.

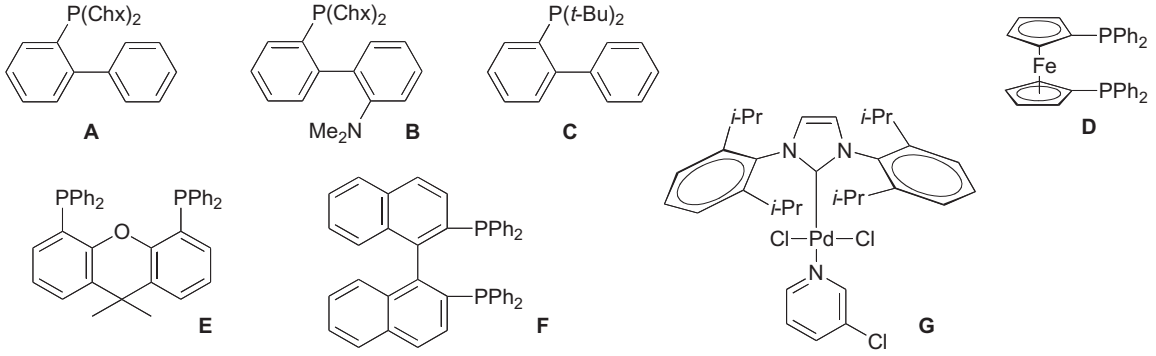
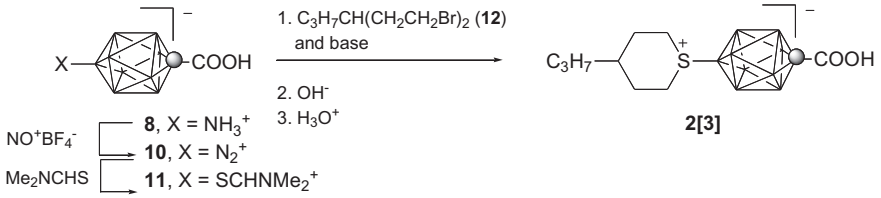
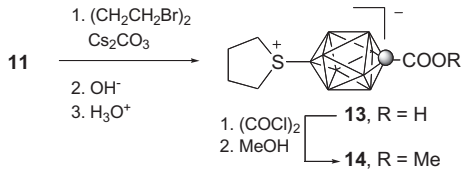


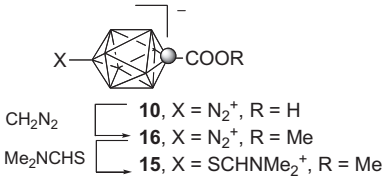
Chart 1.



Scheme 4. Preparation of acid **2[3]**.



Scheme 5. Preparation of methyl ester **14**.



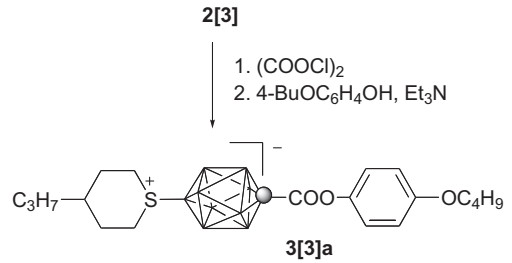
Scheme 6. Preparation of methyl ester **15**.

Ester **3**[**3**]**a** and also methyl ester **3**[**3**]**b** and acid **2**[**3**] exist in solutions as mixtures of interconverting *trans* and *cis* isomers due to low epimerization barrier at the sulfur center [6] (Fig. 3). This is evident from NMR spectra that show two sets of signals in about 4:1 ratio. The lower intensity signals are attributed to the *cis* isomer in which the B(10) nucleus is upfield by 2 ppm. In the *cis* isomer of **3[3]a** the hydrogen atoms of the two methylene groups adjacent to the sulfonium center are moved from their positions at 3.43 ppm (br t) and 3.71 (br doublet) in the *trans* isomer to form a multiplet centered at about 3.55 ppm. The carboxyl group substituent is also affected by epimerization at the sulfur atom. Thus, the methyl group in ester **3[3]b** is deshielded by 0.004 ppm in the *cis* isomer.

3. Conclusions

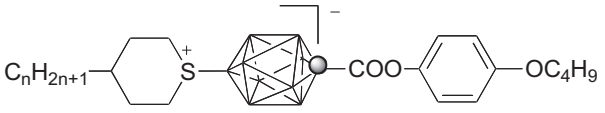
We have developed a practical, large-scale preparation of acid [*closo*-2-CB_9H_9-2-COOH]$^-$ (**4**) primarily by reducing the volume of the aqueous phase and better control of reaction temperature. The new procedure was demonstrated on a 40 g scale of $B_{10}H_{14}$, which can be run conveniently in a 3-L vessel. The overall yield of the iodo acid **1** typically is about 10–12 g or 8–10% from 40 g of $B_{10}H_{14}$, which is essentially the same as previously reported for 4 g of $B_{10}H_{14}$.

Our search for a more efficient Pd catalyst was unsuccessful, and the amination procedure for iodo acid **1** that gives about 50% of amino acid **8** could not be improved. The cycloalkylation reaction and formation of the sulfonium acid **2[n]** was improved by using Cs_2CO_3 as the base, nevertheless the yield remains under 50%. The overall yield of the sulfonium acid **2[3]** from the iodo acid **1** was about 13%. Thus, 1.3 g of **2[3]** can be obtained from 40 g of $B_{10}H_{14}$. Further increase of the overall yield can be achieved by improving the amination and cycloalkylation steps, and complete separation of the isomeric iodo acids.



Scheme 8. Preparation of ester **3**[**3**]**a**.

Table 3
Transition temperatures (°C) and enthalpies (kJ) for **3**[**n**]**a**.[a]



n		
3	Cr 111	(N 96) I
	29.3	*1.1*
5	Cr 101	(N 97) I[b]
	28.6	*0.6*

[a] Cr – crystal, N – nematic, I – isotropic. Monotropic transitions in parentheses. Transition enthalpies are given below in italics.
[b] Ref. [6].

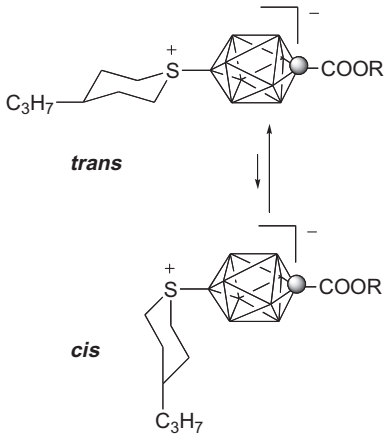
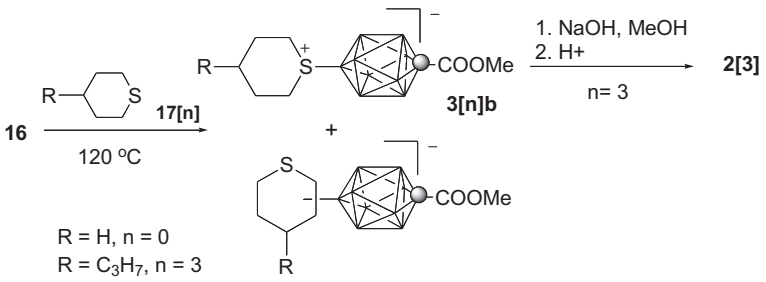


Fig. 3. Interconversion of the *trans* and *cis* isomers of esters of ester **3**[**3**]. Two major conformers are shown.



Scheme 7. Preparation of methyl esters **3**[**n**]**b** and acid **2**[**3**].

4. Experimental

Reagents, excluding decaborane, and solvents were obtained commercially and used as supplied. KOH and HCl solutions were pre-chilled in the freezer (−10 – −20 °C) before use. Reactions and subsequent manipulations were conducted in air. NMR spectra were obtained at 400.1 MHz (^{1}H) or 128.4 MHz (^{11}B) in CD_3CN, unless specified otherwise. ^{1}H NMR spectra were referenced to the solvent signals, while ^{11}B NMR chemical shifts were referenced to an external boric acid sample in CH_3OH that was set to 18.1 ppm.

4.1. Purification of decaborane ($B_{10}H_{14}$)

Technical grade decaborane (200 g, 1.64 mol) was suspended in CH_2Cl_2/hexane (1:9, 300 mL) and passed through a silica gel plug (6 × 6 in.), which was continuously washed with CH_2Cl_2/hexane (1:9) until mass recovery was constant (176 g, 88%). The decaborane was further purified by vacuum sublimation (100–110 °C, 0.5 mm Hg) onto a cold finger. A light yellow residue was left over in some cases. Mass recovery was greater than 95% for sublimation.

4.2. Preparation of [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ [NMe_4]$^+$ (**1**) and [*closo*-1-CB_9H_8-1-(COOH)-6-I]$^-$ [NMe_4]$^+$ (**7**) [4]

A solution of [*closo*-2-CB_9H_8-2-COOH-7-I]$^-$ [NEt_4]$^+$ (**6**, 38.48 g, 0.091 mol) in CH_3CN (150 mL) was refluxed for 22 h. Solvent was removed *in vacuo*, 10% HCl (275 mL) was added, and the mixture was extracted with Et_2O (4 × 100 mL). Water (350 mL) was added to the combined Et_2O extracts, and the solvent was completely removed *in vacuo*. The resulting suspension was filtered, [NMe_4]$^+$Cl$^-$ (11.05 g, 0.101 mol) was added, and the white precipitate was filtered off, washed with H_2O (3 × 100 mL), press dried, and further dried overnight in air giving 22.5–28.5 g (68–86% yield) of a 3:2 mixture of iodo acids **1** and **7** based on ^{11}B NMR, which was consistent with that reported in the literature [4].

4.3. Isolation of [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ [NMe_4]$^+$ (**1**) [4]

A 3:2 mixture of iodo acids **1** and **7** (25.74 g, 0.071 mol) was suspended in near boiling H_2O (250 mL). EtOH (120 mL) was added slowly until the solution became homogeneous. The solution was further heated until solid material began to develop, and then a minimal amount of EtOH (~10 mL) was added to completely redissolve the material. The solution was removed from heat, and left to cool to ambient temperature at which white needles began to grow. The needles were filtered, washed with a small amount of water (50 mL), and dried in air. The needles were recrystallized a second time giving 10.8–14.7 g of 99% pure isomer (42–57% yield). ^{11}B NMR was consistent with that reported in the literature [4]. The combined filtrates from the two recrystallizations contained a 2:3 ratio of iodo acids **1** and **7** by ^{11}B NMR.

4.4. Preparation of [*closo*-1-CB_9H_8-1-COOH-10-(4-$C_3H_7C_5H_9S$)] (**2[3]**)

4.4.1. Method A

A crude protected mercaptan [*closo*-1-CB_9H_8-1-COOH-10-$SCHNMe_2$] (**11**, 2.00 g, 7.90 mmol) was added to a solution of Cs_2CO_3 (10.29 g, 31.6 mmol) and [NBu_4]$^+$Br$^-$ (0.255 g, 0.79 mmol) in CH_3CN (200 mL), which resulted in the formation of a white precipitate. 1,5-Dibromo-3-propylpentane (**12**, 2.22 mL, 11.84 mmol) [14] was added and the reaction mixture was stirred for 24 h at 85 °C. The reaction mixture was evaporated to dryness, the residue dissolved in a MeOH solution (50 mL) containing NaOH (0.304 g, 7.59 mmol) and the mixture was stirred at 55 °C for 4 h, to hydrolyze the ester by-product. Water was added (20 mL), the solvent was removed nearly to dryness, and 10% HCl (300 mL) was added. The suspension was stirred vigorously with Et_2O (50 mL) until the aqueous layer became homogeneous. The Et_2O layer was separated, and the aqueous layer was further extracted with Et_2O (4 × 50 mL). The Et_2O layers were combined, washed with water, dried (Na_2SO_4), and evaporated leaving crude sulfonium acid **2[3]** as an orange solid. The material was passed through a short silica gel plug (CH_3OH/CH_2Cl_2, 1:19, R_f = 0.4), solvent evaporated, and the residue washed with hot hexane giving 1.67–2.08 g of an off-white solid. The solid was recrystallized from EtOH or MeOH to give 1.09–1.13 g (45–47% yield) of pure acid **2[3]** as colorless needles. Crystallization from toluene gave colorless blades of acid **2[3]** as a solvate with toluene (1:1) from which the solvent was removed by heating at 100 °C in vacuum for 2 h: m.p. 252–254 °C; ^{1}H NMR major signals: δ 0.6–2.6 (br m, 8H), 0.93 (t, J = 7.1 Hz, 3H), 1.31–1.45 (m, 4H), 1.64–1.75 (m, 2H), 2.05–2.15 (m, 1H), 2.33 (dm, J = 11.8 Hz, 2H), 3.39 (t, J = 12.4 Hz, 2H), 3.74 (dm, J = 12.0 Hz, 2H), 9.7 (brs, 1H); minor signals: δ 2.29–2.33 (m), 3.47–3.56 (m); ^{11}B NMR δ major signals: −20.3 (d, J = 141 Hz, 4B), −14.8 (d, J = 158 Hz, 4B), 32.4 (s, 1B); minor signal: δ 30.3 (s). *Anal.* Calc. for $C_{10}H_{25}B_9O_2S$: C, 39.17; H, 8.22. Found: C, 39.61; H, 8.11%.

4.4.2. Method B

A solution of methyl ester **3[3]b** (0.88 g, 2.74 mmol) and NaOH (0.44 g, 11 mmol) in MeOH (20 mL) was refluxed for 6 h. The solvent was evaporated, water was added followed by 10% solution of HCl. The resulting precipitated was filtered and dried giving 0.71 g (84% yield) of acid **2[3]**.

4.5. Preparation of ester [*closo*-1-CB_9H_8-1-COOH-10-(4-$C_3H_7C_5H_9S$)] and 4-butoxyphenol (**3[3]a**)

Acid (**2**[**3**]) (40 mg, 0.13 mmol) was dissolved in anhydrous CH_2Cl_2 (2 mL). $(COCl)_2$ (0.017 mL, 0.197 mmol) and a catalytic amount of *N*,*N*-dimethylformamide were added, the reaction mixture was stirred for 1 h, and evaporated to dryness *in vacuo*. The residue was dissolved in anhydrous CH_2Cl_2 (5 mL) and NEt_3 (0.11 mL, 0.784 mmol) and 4-butoxyphenol (33 mg, 0.20 mmol) were added. The reaction was stirred overnight. The reaction mixture was washed with 5% HCl, organic layer dried (Na_2SO_4), and solvent removed. The crude material was passed through a short silica gel plug (CH_2Cl_2/hexane, 1:1) giving 47 mg (52% yield) of ester **3[3]a** as a white crystalline solid. The resulting ester was purified further by recrystallization from *iso*-octane/toluene: ^{1}H NMR ($CDCl_3$) δ 0.6–2.8 (br m, 8H), 0.95 (t, J = 6.8 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H), 1.36–1.43 (m, 4H), 1.51 (sextet, J = 7.5 Hz, 2H), 1.65–1.83 (m, 4H), 2.26–2.42 (m, 3H), 3.43 (t, J = 12.6 Hz, 2H), 3.71 (br d, J = 12.7 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H); minor signals: δ 2.07–2.14 (m), 2.24–2.35 (m), 3.54–3.61 (m); ^{11}B NMR ($CDCl_3$) major signals: δ −19.6 (d, J = 146 Hz, 4B), −14.0 (d, J = 160 Hz, 4B), 31.7 (s, 1B); minor signal: δ 30.0 (s). *Anal.* Calc. for $C_{20}H_{37}B_9O_3S$: C, 52.81; H, 8.20. Found: C, 52.00; H, 8.07%.

4.6. Preparation of [*closo*-1-CB_9H_8-1-COOMe-10-($C_5H_{10}S$)] (**3[0]b**)

A solution of ester [*closo*-1-CB_9H_8-1-COOMe-10-N_2] (**16**, 20 mg, 0.09 mmol), prepared by methylation of dinitrogen acid **10** with CH_2N_2 [9], in thiane (1 mL) was heated at 120 °C for 2 h. The solvent was removed under reduced pressure (80 °C, 0.2 mm Hg), the residue was washed with hexane, and separated using a short silica gel column (hexane/CH_2Cl_2, 1:1). The first fraction contained 17.3 mg (64% yield) of pure methyl ester **3[0]b** as a white crystalline solid, which was recrystallized from *iso*-octane: m.p.

173–174 °C; ^{1}H NMR δ 1.20 (br q, J = 144 Hz, 4H), 1.69 (dtt, J_1 = 11.6 Hz, J_2 = 11.0 Hz, J_3 = 3.0 Hz, 1H), 1.89–1.95 (m, 1H), 1.90 (br q, J = 157 Hz, 4H), 1.98–2.08 (m, 2H), 2.33 (dm, J = 12.0 Hz, 2H), 3.38 (ddd, J_1 = 12.9 Hz, J_2 = 12.3 Hz, J_2 = 2.5 Hz, 2H), 3.68 (dt, J_1 = 12.4 Hz, J_2 = 2.4 Hz, 2H), 3.96 (s, 3H); ^{11}B NMR δ −20.3 (d, J = 143 Hz, 4H), −14.8 (d, J = 158 Hz, 4H), 32.2 (s, 1H). HRMS, calcd for $C_8H_{22}B_9O_2S$ m/z 281.2178; found m/z 281.2198.

The more polar fraction (6.3 mg) was eluted with CH_2Cl_2: ^{1}H NMR (CD_3CN) δ major signal 3.96 (s); ^{11}B NMR (CD_3CN) major signals δ −24.5 (d, J = 135 Hz, 4B), −18.5 (d, J = 156 Hz, 4B), 48.0 (s, 1B). HRMS, calcd for $C_8H_{22}B_9O_2S$ m/z 281.2175; found m/z 281.2215.

4.7. Preparation of [closo-1-CB_9H_8-1-COOMe-10-(4-$C_3H_7C_5H_9S$)] (**3[3]b**)

4.7.1. Method A

A solution of methyl ester **16** (250 mg, 1.22 mmol) in 4-propylthiane (**17[3]**, 2.0 mL) was stirred at 120 °C for 3 h. Excess thiane was removed and the semisolid residue was passed through a silica gel plug (hexane/CH_2Cl_2, 1:2). The first fraction containing the product was evaporated giving 192 mg (49% yield) of ester **3[3]b** as a white solid.

4.7.2. Method B

Crude acid **2[3]** (2.40 g, 7.8 mmol), obtained by hydrolysis of the reaction products as described in Section 4.4. Method A, was dissolved in CH_2Cl_2 (20 mL) and $(COCl)_2$ (2.60 mL, 30 mmol) was added followed by a catalytic amount of DMF. The mixture was stirred for 1 h at ambient temperature, volatiles were removed, the resulting acid chloride was dissolved in MeOH (20 mL) and the solution was gently refluxed for 1 h. MeOH was evaporated and the crude methyl ester **3[3]b** was purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 1:1) to give 1.47 g (58% yield) of **3[3]b** as a white solid, which was recrystallized from hexane/CH_2Cl_2: m.p. 95–103 °C; ^{1}H NMR major signals: δ 0.60–2.50 (m, 8H), 0.93 (t, J = 7.0 Hz, 3H), 1.27–1.45 (m, 4H), 1.65–1.75 (m, 2H), 2.04–2.15 (m, 1H), 2.33 (dm, J = 11.8 Hz, 2H), 3.39 (t, J = 11.9 Hz, 2H), 3.74 (dm, J = 12.2 Hz, 2H), 3.956 (s, 3H); minor signals: δ 3.47–3.56 (m), 3.960 (s); ^{11}B NMR major signals: δ −20.3 (d, J = 141 Hz, 4B), −14.8 (d, J = 158 Hz, 4B), 32.6 (1B); minor signal: δ 30.6 (s). *Anal.* Calc. for $C_{11}H_{27}B_9O_2S$: C, 41.20; H, 8.49. Found: C, 41.40; H, 8.60%.

4.8. Preparation of [closo-2-CB_9H_9-2-COOH]$^-$ [NEt_4]$^+$ (**4**)

[*Arachno*-6-CB_9H_{13}-6-COOH]$^-$ [NEt_4]$^+$ (**5**, 64.5 g, 0.217 mol) was suspended in a biphasic system of Et_2O (500 mL) and ice-cold 18% HCl (400 mL) in a 2-L Erlenmeyer flask. The mixture was stirred vigorously in an ice-bath and slowly warmed to room temperature until only traces of solid remained (~2 h). The Et_2O was separated in a 2-L separatory funnel, and the aqueous layer was further extracted with additional Et_2O (3 × 150 mL). Any remaining solid material was drained into the aqueous layer. The Et_2O layers were combined in a 1-L round-bottom flask and evaporated to approximately one-half its volume. A cooled (0 °C) solution of KOH (2.7 M, 645 mL) was then added, and the remaining Et_2O was removed, and the last remnants of Et_2O were removed in vacuum (<5 mm Hg) until vigorous bubbling was no longer observed. The solution was then poured into a 3-L three-necked flask equipped with an addition funnel and mechanical stirrer and cooled down to ~5 °C in an ice-bath. Elemental I_2 (126.5 g, 0.500 mol) was slowly added in ~10 g portions every 5–10 min, or as often as solid iodine was no longer visible. Towards the last few additions, the solution developed a yellow/orange color. The solution was further stirred for 1 h where the yellow/orange color dissipated after ~30 min. Reaction progress was monitored by following ^{11}B NMR spectrum of an aliquot taken directly from the reaction mixture [^{11}B {^{1}H} NMR (D_2O) δ −1.2 (1B), −3.8 (1B), −23.3 (1B), −26.5 (2B), −29.4 (2B), −30.3 (2B)]. Solid $Na_2S_2O_5$ (123.8 g, 0.651 mol) and [NEt_4]$^+$Br$^-$ (68.41 g, 0.3255 mol) were then added, and after 15 min, 20% HCl (85 mL) was added slowly via the addition funnel until a pH of ~3 was obtained. A white precipitate was filtered, washed with water (5 × 100 mL), press dried, and further dried in air overnight giving 27–37 g (42–58% yield) of [*closo*-2-CB_9H_9-2-COOH]$^-$ [NEt_4]$^+$ (**4**) in purity greater than 90% by ^{11}B NMR. The filtrate is a yellow solution. ^{11}B NMR was consistent with that reported in the literature [10,11].

4.9. Preparation of [arachno-6-CB_9H_{13}-6-COOH]$^-$ [NEt_4]$^+$ (**5**)

Glyoxylic acid (200.0 g, 2.16 mol) was slowly added in 15 g portions to a cooled solution (0 °C) of KOH (251.3 g, 4.48 mol) in water (300 mL) containing 200 g of crushed ice in a 3-L three-necked flask equipped with an addition funnel, mechanical stirrer, and internal thermometer. Vigorous stirring and slow addition of glyoxylic acid is important to maintain the temperature of the solution below 5 °C. Finely crushed $B_{10}H_{14}$ (40.0 g, 0.327 mol) was then slowly added in two portions, while maintaining the temperature of the solution around 5 °C. Once all $B_{10}H_{14}$ had dissolved, the solution was vigorously stirred for an additional 2 h (<5 °C). Reaction progress was monitored by following ^{11}B NMR spectrum of an aliquot taken directly from the reaction mixture [^{11}B {^{1}H} NMR (D_2O) δ −3.2 (1B), −4.7 (2B), −14.6 (1B), −16.2 (1B), −19.8 (1B), −20.8 (1B), −26.7 (1B), −38.3 (1B), −38.7 (1B)]. Solid [NEt_4]$^+$Br$^-$ (47.9 g, 0.228 mol) was added, and after 10 min, freezer-cold (−15 °C) 20% solution of HCl (340 mL) was slowly added via the addition funnel until a pH of ~3 was obtained. Addition of HCl resulted in vigorous bubbling, foaming, and release of H_2. Occasionally, manual breaking up of large clumps of the product was necessary for thorough neutralization of the product and decomposition of the flammable boron hydride byproducts. At pH ~3, the bubbling and foaming begins to subside. The resulting white precipitate was filtered, washed with H_2O (10 × 100 mL), press dried, and further dried in air overnight giving 64–72 g (66–74% yield) (see footnote 1) of [*arachno*-6-CB_9H_{13}-6-COOH]$^-$ [NEt_4]$^+$ (**5**) in purity greater than 90% by NMR: ^{11}B {^{1}H} NMR (CD_3CN) δ major signals −0.5 (1B), −9.2 (3B), −20.1 (1B), −27.8 (1B), −39.0 (2B); (acetone-d_6) δ major signals −0.3 (1B), −9.0 (2B), −9.6 (1B), −19.6 (1B), −27.6 (1B), −38.8 (2B) [lit. [10] (acetone-d_6) −0.6 (1B), −9.4 (1B), −10.3 (3B), −19.3 (1B), −27.9 (2B), −39.1 (1B)].

When an acetone solution of **5** is filtered, evaporated, and redissolved in acetone-d_6 the spectrum changes: ^{11}B {^{1}H} NMR (acetone-d_6) δ major signals 3.0 (2B), 0.5 (1B), −4.6 (2B), −11.9 (2B), −29.1 (1B), −36.2 (1B).

4.10. Preparation of [closo-2-CB_9H_8-2-COOH-7-I]$^-$ [NEt_4]$^+$ (**6**) [4]

A red solution of *N*-iodosuccinimide (35.23 g, 0.157 mol) and [*closo*-2-CB_9H_9-2-COOH]$^-$ [NEt_4]$^+$ (**4**, 30.82 g, 0.104 mol) in anhydrous MeCN (150 mL) was stirred vigorously for 1 h at 0 °C and then stored for 72 h in a freezer (−10 to −20 °C). MeCN was removed at 0 °C under reduced pressure (<10 mm Hg). Solid $Na_2S_2O_5$ (29.8 g, 0.157 mol) and 10% HCl (350 mL) were added and the reaction mixture turned green/yellow and a yellow precipitate began to form. If solution does not turn green/yellow, more $Na_2S_2O_5$ should be added. The mixture was stirred vigorously. Once all red residue dissolved, Et_2O (100 mL) was added and the mixture was vigorously stirred until the yellow precipitate redissolved leaving an orange organic layer. The Et_2O layer was separated and the aqueous layer was further extracted with Et_2O

(4 × 100 mL). The Et_2O layers were combined, and half of the Et_2O was evaporated before adding H_2O (250 mL). The remaining Et_2O was evaporated completely and the aqueous solution was filtered to remove insoluble material. Solid $[NEt_4]^+Br^-$ (32.91 g, 0.157 mol) was added and a white solid begin to precipitate after brief stirring. The solid was filtered, washed with H_2O (5 × 100 mL), press dried and further dried in air overnight giving 28–40 g (68–91% yield) of iodo acid **6**. ^{11}B NMR was consistent with that reported in the literature [4]. In addition, NMR revealed that up to 20% of the expected product **6** has undergone rearrangement giving the 1,10 and 1,6 isomers of iodo acid **1** and **7** in about 2:1 ratio. The product was used for the next step.

4.11. Preparation of [closo-1-CB_9H_8-1-COOH-10-NH_3] (**8**) [9]

Following a literature procedure [9], [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ $[NMe_4]^+$ (**1**, 15.00 g, 0.041 mol) was added to a solution of lithium hexamethyldisilazane (LiHMDS, 618 mL, 0.615 mol, 1.0 M in THF) at ambient temperature under N_2. The light orange suspension was stirred vigorously for 20 min or until the suspension became more fine and disperse. Pd_2dba_3 (0.756 g, 0.83 mmol) and 2-(dicyclohexylphosphino)biphenyl (**A**, 0.985 g, 3.30 mmol) were added, and the reaction was stirred at reflux for 20 h. After several minutes at reflux, the reaction mixture turned dark brown. The reaction was cooled to 0 °C, and 10% HCl (1500 mL) was added slowly. The THF was removed *in vacuo* giving a dark orange solution. The orange solution was extracted with Et_2O (5 × 200 mL), the Et_2O layers were combined, dried (Na_2SO_4), and evaporated at slightly elevated temperature (~40 °C) to ensure complete removal of trimethylsilanol. ^{11}B NMR of the crude material revealed a 7:3 ratio of amino acid **8** to parent acid **9**.

The crude brown/orange material was redissolved in Et_2O, and water (150 mL) was added. The Et_2O was removed *in vacuo* or until bubbling became less vigorous. The aqueous layer was filtered through celite, and the process was repeated two more times (the insoluble material presumably contains a B(10)-phosphonium derivative). Water (3 × 100 mL) was added to the flask and the flask was shaken vigorously to release the remaining amino acid from the insoluble material. The aqueous fractions were filtered as well. The aqueous layers were combined, and $[NEt_4]^+Br^-$ (8.67 g, 0.041 mol) was added resulting in precipitation of a white solid. CH_2Cl_2 (400 mL) was added, and the biphasic system was stirred vigorously overnight until the aqueous layer became clear. The organic layer was separated, and the process was repeated once more. The biphasic system was stirred for 1 h. The H_2O layer was filtered, reacidified with conc. HCl (75 mL), and extracted with Et_2O (5 × 150 mL). The Et_2O layers were combined, washed with water, dried (Na_2SO_4), and solvent evaporated giving 3.55–4.14 g (48–56% yield) of amino acid **8** with purity >90% by ^{11}B NMR. The amino acid was used for the next step without further purification.

4.12. Preparation of [closo-1-CB_9H_8-1-COOH-10-N_2] (**10**) [9]

Amino acid [*closo*-1-CB_9H_8-1-COOH-10-NH_3] (**8**, 1.850 g, 10.31 mmol) was suspended in anhydrous CH_3CN (20 mL) and anhydrous pyridine (4.25 mL, 51.5 mmol) was added. The reaction mixture was cooled to −15 °C, and $NO^+[BF_4]^-$ (3.61 g, 30.9 mmol) was added in six portions at 10 min intervals. Once all $NO^+[BF_4]^-$, was added, the reaction was stirred for 1.5 h at −15 °C.

The reaction mixture was evaporated to dryness (the flask was kept at cold water bath), 10% HCl (200 mL) was added, and the mixture was stirred vigorously until all solids had dissolved (~20 min). The aqueous solution was extracted with Et_2O (4 × 50 mL), the Et_2O layers were combined, washed with water, dried (Na_2SO_4), and evaporated to dryness giving 1.327 g of crude dinitrogen acid **10**. The crude product was passed through a short silica gel plug (CH_3OH/CH_2Cl_2, 1:19, R_f = 0.2) giving 0.97–1.29 g (49–65% yield) of dinitrogen acid **10** as a white solid.

4.13. Preparation of [closo-1-CB_9H_8-1-COOH-10-SCHNMe_2] (**11**) [9]

A solution of acid [*closo*-1-CB_9H_8-1-COOH-10-N_2] (**10**, 1.678 g, 8.81 mmol) and freshly distilled Me_2NCHS (11.50 mL, 0.132 mmol) was stirred at 120 °C for 1 h. As the reaction progressed, bubbling of N_2 became evident. Excess Me_2NCHS was removed by vacuum distillation (120 °C, 1.0 mm Hg) leaving crude product as an off-white crystalline solid. The crude product was washed with toluene giving 2.00–2.16 g (91–98% yield) of crude protected mercaptan **11** containing up to 5% of Me_2NCHS by ^1H NMR.

4.14. Preparation of [closo-1-CB_9H_8-1-COOMe-10-(4-C_4H_8S)] (**14**)

The ester was prepared from **11** and 1,4-dibromobutane followed by treatment with $(COCl)_2$ and MeOH. Pure ester **14** was isolated as a white solid by chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) followed by recrystallization (CH_2Cl_2/hexane): mp 114–116 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.30 (q, J = 142 Hz, 4H), 2.03 (q, J = 158 Hz, 4H), 2.28–2.37 (m, 2H), 2.58–2.67 (m, 2H), 3.67–3.76 (m, 2H), 3.78–3.88 (m, 2H), 4.02 (s, 3H); ^{11}B {^1H} NMR δ −20.0, −14.8, 34.1. *Anal.* Calc. for $C_7H_{19}B_9O_2S$: C, 31.78; H, 7.24. Found: C, 31.88; H, 7.32%.

4.15. Preparation of 4-propylthiane (**17[3]**) [15]

To a solution of dibromide **12** (9.8 g, 36.0 mmol) [14] in EtOH (80 mL) a solution of $Na_2S{\cdot}9H_2O$ (13.0 g, 54 mmol) in water (40 mL) was added dropwise during 1 h at 50 °C. The mixture was stirred at this temperature for 1 h, then refluxed for 1 h, and diluted with water. The organic product was extracted with hexanes, extract dried (Na_2SO_4) and solvent evaporated. The oily residue was passed through silica gel plug to give 4.50 g of thiane (87% yield) as a colorless oil. Analytical sample was obtained by bulb-to-bulb distillation (50–55 °C, 0.5 mm Hg; lit. [15] b.p. 92 °C/23 mm Hg): ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 7.2 Hz, 3H), 1.16–1.23 (m, 2H), 1.24–1.37 (m, 5H), 1.98 (br d, J = 11.9 Hz, 2H), 2.58 (br d, J = 11.9 Hz, 2H), 2.65 (t, J = 12.6 Hz, 2H).

4.16. Preparation of 4-pentylthiane (**17[5]**) [15,16]

The thiane was prepared in 85% yield from 1,5-dibromo-3-pentylpentane [14] using method similar to that described for **17[3]**: b.p. 52–53 °C, 0.15 mm Hg (lit. [16] b.p. 101 °C, 2 mm Hg); ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.16–1.45 (m, 11H), 1.99 (br d, J = 12.1 Hz, 2H), 2.58–2.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 26.0, 28.8, 32.05, 34.2, 37.2, 37.3; EI-MS, *m/z* 172 (M, 49) 115 (100).

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