Boron Cluster Anions

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Functionalization of *closo*-Borates via Iodonium Zwitterions**

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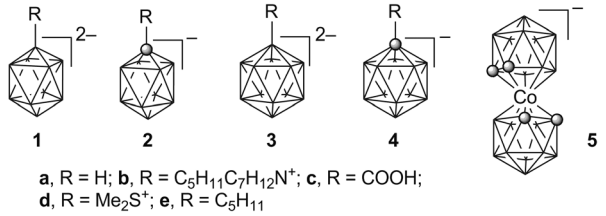
Dedicated to Professor Russell Grimes on the occasion of his 80th birthday

Abstract: *A simple method for the functionalization of closo-borates [closo-$B_{10}H_{10}$]$^{2-}$ (**1**), [closo-1-CB_9H_{10}]$^-$ (**2**), [closo-$B_{12}H_{12}$]$^{2-}$ (**3**), [closo-1-$CB_{11}H_{12}$]$^-$ (**4**), and [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ (**5**) is described. Treatment of the anions and their derivatives with ArI(OAc)$_2$ gave aryliodonium zwitterions, which were sufficiently stable for chromatographic purification. The reactions of these zwitterions with nucleophiles provided facile access to pyridinium, sulfonium, thiol, carbonitrile, acetoxy, and amino derivatives. The synthetic results are augmented by mechanistic considerations.*

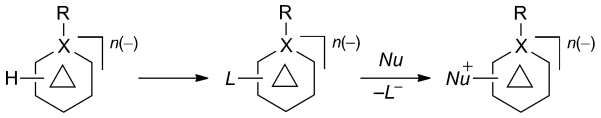
Closo-Borates, such as **1**–**4** (Scheme 1),[1] and metallaborates (e.g. **5**)[2] are becoming increasingly important for the development of new materials and pharmacophores as a result of their steric and electronic properties, low metabolic reactivity,



Scheme 1. *closo*-Borates used in this study. Spheres represent a C–H fragment, and all other vertices are B–H fragments.

hydrophobic properties, and highly delocalized negative charges.[3] For example, they have been used as structural elements of polar and ionic liquid crystals,[4] proposed as elements of nanoscale construction sets,[5] investigated as pharmacophores,[6] and are components of boron neutron capture therapy (BNCT) technology.[6a,7] In spite of favorable properties and a great deal of previously discovered chemistry,[8] controlled functionalization of the boron atoms and the range of accessible functional groups in **1**–**5** still remain problematic.

The regiospecific functionalization of boron atoms in *closo*-borates typically relies on a leaving group *L* that serves as a synthetic handle for the introduction of other functionalities (Scheme 2).[9] One synthetically important group is the



Scheme 2. Functionalization of *closo*-borates. X = B (*n* = 2), X = C (*n* = 1).

iodo group (*L* = I), introduced by direct iodination. However, iodination of the clusters often leads to ionic regioisomers that are difficult to separate,[4b] and subsequent synthetic transformations of iodo derivatives are limited to palladium-catalyzed coupling reactions.[10] Another versatile group is the dinitrogen substituent ($L = N_2^+$); unfortunately, stable and synthetically useful examples of such zwitterions are limited to the apical derivatives of 10-vertex *closo*-borates **1** and **2**. Dinitrogen derivatives of the [*closo*-$B_{10}H_{10}$]$^{2-}$ anion (**1**) are obtained by a direct diazotization/reduction sequence[11] or by an elegant diazo-transfer process[4e,12] in moderate yields. In contrast, apical dinitrogen derivatives of the [*closo*-1-CB_9H_{10}]$^-$ anion (**2**) are obtained through the diazotization of amines.[13] The dinitrogen group can be readily replaced with a nucleophile in a S_N1-type process involving a boronium ylide by heating in the reagent/solvent. Such reactions permit the efficient introduction of mercapto, sulfido, acetamido, amino, carbonyl, and *N*-pyridinyl functionalities or their equivalents at the apical positions of the 10-vertex anions.[4e,11–13] Unfortunately, dinitrogen zwitterions of equatorial derivatives of the 10-vertex clusters **1** and **2** and 12-vertex analogues **3** and **4** have extremely limited use owing to their insufficient stability.[4b,14]

We now report that aryliodonium zwitterions ($L = ArI^+$) provide a general synthetic handle for the 10- and 12-vertex *closo*-borates **1**–**4**, and for metallacarborates, such as **5**. The preparation of the aryliodonium zwitterions was straightforward, and they reacted with a wide range of nucleophiles (Scheme 2). Initially, we focused on [*closo*-$B_{10}H_9$-1-IPh]$^-$ (**6a**),[15] the only reported aryliodonium zwitterion of

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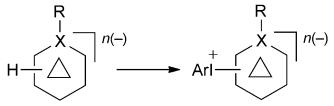
a *closo*-borate.[16] Attempts to reproduce the original synthesis[15] (**1a[2NH$_4$]**, PhIO, H_2O/CH_3CN, steam bath) were unsuccessful; at best, the product was obtained in impure form in low yield. By a systematic approach, we discovered that the treatment of a solution of **1a[2NH$_4$]** in aqueous acetic acid (70%) with solid $PhI(OAc)_2$ (1 equiv) at 0°C in the presence of $[NEt_4]^+$ immediately resulted in the formation of a white precipitate, from which **6a[NEt$_4$]** was obtained in 46% yield by SiO_2 chromatography (Table 1, entry 1). During the preparation of **6a[NEt$_4$]**, the 1,10-bisphenyliodonium zwitterion **7** was isolated as a minor component (7%). However, the same reaction conducted with 2 equivalents of $PhI(OAc)_2$ or PhI(OH)(OTs) (Ts = *p*-toluenesulfonyl) gave **7** as the sole product in 82% yield (Table 1, entry 2). A similar reaction of the 1-quinuclidinium derivative **1b[NMe$_4$]**[4e] with $PhI(OAc)_2$ in MeCN gave the 1-phenyliodonium derivative **6b** in 59% yield (Table 1, entry 3).

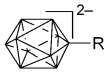
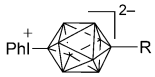
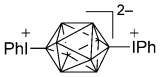
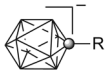
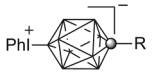
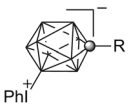
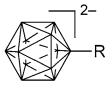
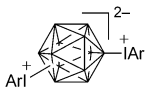
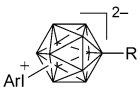
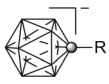
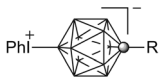
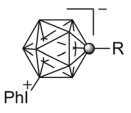
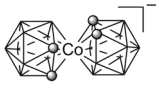
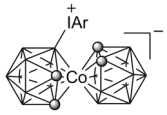
Analysis of the reaction mixture revealed that PhI^+ is fully selective for the apical position of the $[closo\text{-}B_{10}H_{10}]^{2-}$ cluster, and in this respect is similar to ArN_2^+.[12] The regioselectivity of the phenyliodination was investigated for the $[closo\text{-}1\text{-}CB_9H_{10}]^-$ anion (**2a**), which usually exhibits strong preference for equatorial electrophilic substitution.[17] Thus, the treatment of **2a[Cs]** with $PhI(OAc)_2$ (1 equiv) in aqueous AcOH gave a 2:5 mixture of **8a-*p*** and **8a-*m*** in 93% yield (Table 1, entry 4). This ratio of isomers is the highest ever observed for the electrophilic substitution of **2a**. Unfortunately, these regioisomers could not be separated by chromatography or crystallization. Similar results were observed for the phenyliodination of the $[closo\text{-}1\text{-}CB_9H_9\text{-}1\text{-}COOH]^-$ anion (**2c**), for which a 1:2 mixture of **8c-*p*** and **8c-*m*** was obtained in 95% yield (Table 1, entry 5).

The phenyliodination reaction was extended to $[closo\text{-}B_{12}H_{12}]^{2-}$. In aqueous AcOH, the treatment of **3a[2Na]** with $PhI(OAc)_2$ (2 equiv) gave no product, whereas in aqueous trifluoroacetic acid (TFA), a precipitate of the bis-zwitterions **9** was obtained in 69% yield (Table 1, entry 6). The product, presumably a mixture of two regioisomers, was only sparingly soluble in typical solvents. To remedy this problem, we added a methoxy substituent to $PhI(OAc)_2$. The subsequent reaction of $[closo\text{-}B_{12}H_{12}]^{2-}\,2Na^+$ (**3a[2Na]**) with $4\text{-}MeOC_6H_4I(OAc)_2$ gave a 2:7 mixture of regioisomers **9-*p*** and **9-*m*** ($Ar = 4\text{-}MeOC_6H_4$) in 51% yield (Table 1, entry 7) as a microcrystalline solid that was soluble in typical solvents. The individual isomers **9-*p*** and **9-*m*** could be separated chromatographically, although with mass loss owing to their limited thermal stability in solution.

The $[closo\text{-}B_{12}H_{12}]^{2-}$ anion substituted with a $^+SMe_2$ group [*closo*-

Table 1: Synthesis of iodonium zwitterions **6**–**12**.[a]



Entry	Anion		Product(s) and yield				
							
	1		**6**		**7**		
1	**a**, R = H		46% **[NEt$_4$]**		7%		
2	**a**, R = H		0% **[NEt$_4$]**		82%		
3	**b**, R = $^+$Quin[b]		59%		–		
							
	2		**8-*p***		**8-*m***		
4	**a**, R = H			93%[c]			
5	**c**, R = COOH		27%[d]	95%[c]	–		
							
	3		**9-*p***	**9-*m***	**10-*p***	**10-*m***	
6	**a**, R = H,	Ar = Ph	69%[c]		–		
7		Ar = 4-MeOC$_6$H$_4$	12%	51%[c]	34%	–	
8	**d**, R = $^+$SMe$_2$,	Ar = Ph	–		77%[c]		
9	**d**, R = $^+$SMe$_2$,	Ar = 4-MeOC$_6$H$_4$	–		13%	39%	
							
	4		**11-*p***		**11-*m***		
10	**a**, R = H		81%		11%		
11	**e**, R = C$_5$H$_{11}$		81%		8%		
							
	5		**12**				
12			Ar = Ph, 65%				
13			Ar = 4-MeOC$_6$H$_4$, 51%				

[a] Typical conditions: The *closo*-borane (1.0 mmol) in 70% aqueous AcOH or CF_3COOH (TFA; 12 mL) was treated with $ArI(OAc)_2$ (1.05 or 2.1 mmol) at 0°C, and after 1–2 h the product was filtered from the mixture. [b] Quin = 4-pentylquinuclidine; CH_3CN was used as the solvent. [c] Mixture of two isomers. [d] Yield of the isolated product after thermolysis of the isomeric mixture.

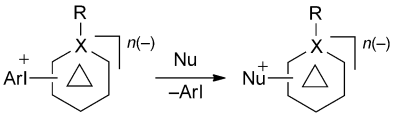
$B_{12}H_{11}$-1-$SMe_2]^-[NEt_4]^+$ (**3d[NEt$_4$]**) also reacted with PhI(OAc)$_2$ in a 5:2 mixture of TFA/CH_2Cl_2 to give two regioisomers, **10d-*p*** and **10d-*m***, which were obtained in a 1:3 ratio and isolated in 77% yield (Table 1, entry 8). Their chromatographic separation was hindered by relatively low solubility, which was improved by the use of 4-$MeOC_6H_4$I(OAc)$_2$ as the reagent, and the individual regioisomers **10d-*p*** and **10d-*m*** (Ar = 4-$MeOC_6H_4$) were then readily isolated (Table 1, entry 9).

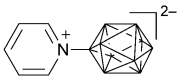
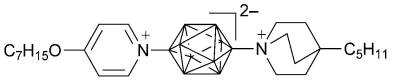
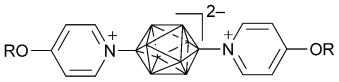
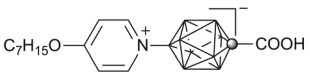
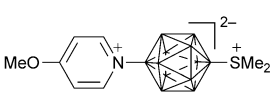
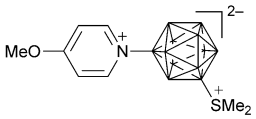
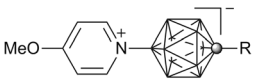
The reaction of [*closo*-1-$CB_{11}H_{12}]^-$ (**4a[Cs]**) with PhI(OAc)$_2$ was successful only in the presence of TFA. Thus, zwitterions **11a-*p*** and **11a-*m*** were isolated in 81 and 11% yield, respectively, by chromatography (Table 1, entry 10). Similar results were obtained for the 1-pentyl derivative **4e[Cs]** (Table 1, entry 11). Finally, the anion [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ (**5**) was aryliodinated with PhI(OAc)$_2$ and 4-$MeOC_6H_4$I(OAc)$_2$ in aqueous TFA to give the 8-aryliodonium species **12** as the sole product in good yield (Table 1, entry 12 and 13).

The aryliodonium zwitterions appeared to be stable in the solid state, but in solution their stability varied depending on the cluster and regioisomer. Thus, ^{1}H NMR spectroscopic analysis of solutions in CD_3CN demonstrated that derivatives of the [*closo*-$B_{12}H_{12}]^{2-}$ anion were least thermally stable and that the 1,7-substituted isomer decomposed faster than the 1,12-substituted analogue: **10d-*m*** underwent 76% decomposition after 2 days at ambient temperature, whereas **10d-*p*** suffered 47% decomposition in the same time period. The aryliodonium derivatives of [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ were moderately unstable, whereas derivatives of the [*closo*-1-$CB_{11}H_{12}]^-$ anion and the 10-phenyliodonium derivatives of [*closo*-1-$CB_9H_{10}]^-$ and [*closo*-$B_{10}H_{10}]^{2-}$ showed no decomposition under ambient conditions over several weeks.[18] In all experiments, PhI or 4-$MeOC_6H_4$I was identified as the major organic product. Full kinetic analysis and single-crystal XRD data for selected iodonium zwitterions will be reported elsewhere. We used the difference in stability of the phenyliodonium regioisomers of [*closo*-1-$CB_9H_{10}]^-$ to prepare the pure carboxylic acid [*closo*-1-CB_9H_8-1-COOH-10-IPh] (**8c-*p***) by thermolysis of the isomeric mixture **8c** in MeCN at 55 °C, followed by simple chromatographic separation of **8c-*p*** from decomposition products of **8c-*m*** (Table 1, entry 5).

Investigation of the reactivity of aryliodonium zwitterions demonstrated their synthetic value for the preparation of functionalized boron clusters. Examples of such reactions with pyridines, sulfur nucleophiles, and other nucleophiles are shown in Tables 2–4. Reactions of aryliodonium zwitterions with pyridine and its 4-alkoxy derivatives at 60–90 °C gave the expected pyridinium products **13**–**19** of nucleophilic replacement of the iodoarene in good to excellent yields (Table 2). The yields observed for **13**–**16**, **18**, and **19** are comparable to or better than those observed when the analogous dinitrogen derivatives were used.[4b,e,12,19] In particular, the preparation of acid **16-*p*** (Table 2, entry 5), an important intermediate for the

Table 2: Reactions of selected iodonium zwitterions with pyridines.[a]



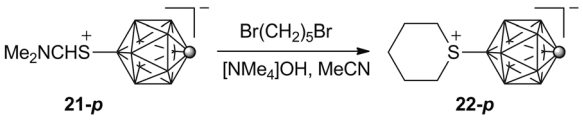
Entry	Zwitterion	Nucleophile	Product(s) and yield	
1	**6a[NEt$_4$]**	pyridine		**13[NEt$_4$]**, 74%[12]
2	**6b**	4-$C_7H_{15}OC_5H_4N$		**14**, 93%[4e]
3	**7**	4-$MeOC_5H_4N$		**15[1]**, R = Me, 57%
4	**7**	4-$C_7H_{15}OC_5H_4N$		**15[7]**, R = C_7H_{15}, 79%[19]
5	**8c-*p***	4-$C_7H_{15}OC_5H_4N$		**16-*p***, 90%
6	**10d**[b]	4-$MeOC_5H_4N$		
			17-*p*, 10%	**17-*m***, 30%
7	**11a-*p***	4-$MeOC_5H_4N$		**18-*p***, R = H, 87%[4b]
8	**11e-*p***	4-$MeOC_5H_4N$		**19-*p***, R = C_5H_{11}, 61%[4b]

[a] Typical conditions: The iodonium zwitterion (1.0 mmol) and appropriate pyridine derivative (2 mL) were stirred at 65–100 °C. [b] Mixture of regioisomers.

synthesis of liquid crystals, was carried out with a fivefold increase in yield as compared to the previous method with a N_2^+ handle and in fewer steps.[4h] Thermolysis of the regioisomeric mixture **10 d** in 4-methoxypyridine, followed by chromatographic separation, gave pure fluorescent pyridinium isomers **17-*p*** and **17-*m***, rare examples of such derivatives[20] of the $[closo\text{-}B_{12}H_{12}]^{2-}$ cluster (Table 2, entry 6).

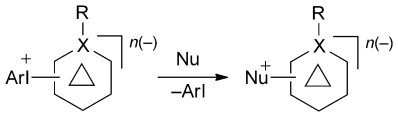
Selected aryliodonium zwitterions were treated with two types of sulfur species: *N*,*N*-dimethylthioformamide, a synthon for the SH group, and thian (Table 3). Thus, reactions of phenyliodonium derivatives **11 a-*p*** and **12** with *N*,*N*-dimethylthioformamide gave the corresponding protected mercaptans **21-*p*** and **23**, the first such derivatives of the $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ cluster and the cobalt dicarbollide,[21] in good yields (Table 3, entries 2 and 4). Reactions of aryliodonium zwitterions with thian permitted direct substitution of the sulfonium fragment on the boron cage. Thus, thermolysis of a regioisomeric mixture of iodonium **8 c** in thian at 90 °C, followed by esterification with CH_2N_2, gave a mixture of sulfonium esters **20**, from which only a small amount of the 10-sulfonium ester **20-*p*** was isolated by recrystallization. Ester **20-*p***, the parent compound of a class of polar liquid crystals,[4c] was obtained in higher yield (81 %) from the isomerically pure carboxylic acid **8 c-*p*** (Table 3, entry 1). This result again represents a significant improvement over the previous method.[22] A similar reaction of the phenyliodonium species **11 a-*p*** with thian gave the sulfonium derivative **22-*p*** in moderate yield (30 %; Table 3, entry 3), along with a product presumably derived from cage arylation with PhI. The same sulfonium derivative, **22-*p***, was cleanly obtained in 73 % yield by the alkylative cyclization of **21-*p*** with 1,5-dibromopentane under hydrolytic conditions (Scheme 3).

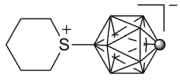
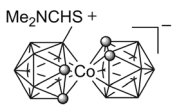
Finally, the regiospecific introduction of three other functional groups to *closo*-borates was demonstrated by



Scheme 3. Preparation of the sulfonium zwitterion **22-*p***.

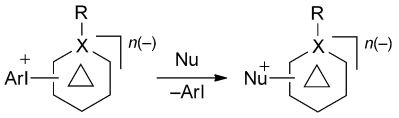
Table 3: Reactions of selected iodonium zwitterions with sulfur nucleophiles.[a]

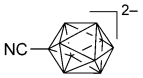
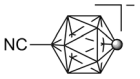
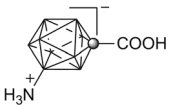
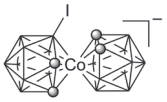
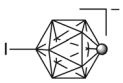


Entry	Zwitterion	Nucleophile	Product and yield
1	**8 c-*p***	$(CH_2)_5S$ (thian)	 **20-*p***, 81 %[b]
2	**11 a-*p***	Me_2NCHS	 **21-*p***, 71 %
3	**11 a-*p***	$(CH_2)_5S$ (thian)	 **22-*p***, 30 %
4	**12**	Me_2NCHS	 **23**, 55 %

[a] Typical conditions: The iodonium zwitterion (1.0 mmol) and the appropriate reagent (2 mL) were stirred at 55–100 °C. [b] The product was isolated after treatment with CH_2N_2.[22]

Table 4: Reactions of selected iodonium zwitterions with other nucleophiles.[a]

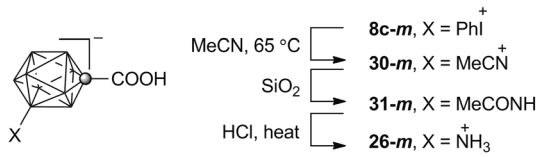


Entry	Zwitterion	Nucleophile	Product and yield
1	**6 a [NEt_4]**	$[NEt_4]^+CN^-$	 **24 [2 NEt_4]**, 71 %
2	**11 a-*p***	$[NEt_4]^+CN^-$	 **25-*p* [NEt_4]**, 65 %[23]
3	**8 c-*m***	MeCN	 **26-*m***, 54 %[b][14]
4	**7**	$[NEt_4]^+[AcO]^-$	 **27 [NEt_4]**, 60 %[c]
5	**12** Ar = 4-$MeOC_6H_4$	$[NEt_4]^+CN^-$	 **28 [NEt_4]**, 73 %[24]
6	**11 a-*p***	$C_6H_{13}MgBr$	 **29-*p* [NEt_4]**, 83 %[10a]

[a] Typical conditions: The aryliodonium zwitterion (1.0 mmol) was treated with the reagent (1.1 mmol) in solution. [b] After hydrolysis of the nitrilium zwitterion. [c] A 73 % yield of the product was calculated on the basis of recovered **7**.

treating selected aryliodonium zwitterions with CN^-, AcO^-, and MeCN as synthons for the COOH, OH, and NH_3 groups, respectively (Table 4). Reactions of iodonium **6a[NEt$_4$]** and **11a-*p*** with $[NEt_4]^+CN^-$ at 55 °C gave the corresponding nitriles **24[2NEt$_4$]** and **25-*p*[NEt$_4$]** in good yields, thus opening access to such derivatives of the $[closo\text{-}B_{10}H_{10}]^{2-}$ cluster and simplifying the preparation of **25-*p*[NEt$_4$]**[23] (Table 4, entries 1 and 2). In contrast, a similar cyanation of **12** gave the 8-iodo derivative [8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**28**)[24] as the sole product, instead of the expected nitrile (Table 4, entry 5). Similarly, [*closo*-1-$CB_{11}H_{11}$-12-I]$^-$ (**29-*p***) was cleanly formed in a reaction of the iodonium zwitterion **11a-*p*** with $C_6H_{13}MgBr$ (Table 4, entry 6). A reaction of the bisphenylodonium zwitterion **7** with 1 equivalent of the acetate anion at 60 °C gave the unsymmetrically substituted 1-acetoxy derivative **27[NEt$_4$]**, which was isolated in good yield (Table 4, entry 4).

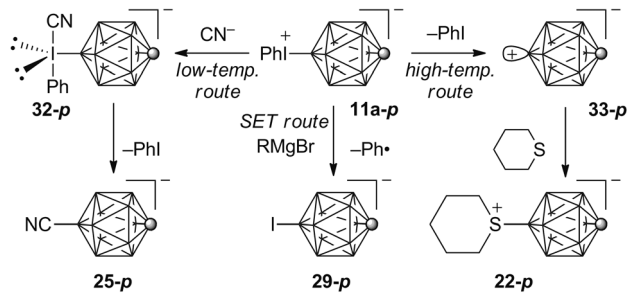
Thermolysis of a mixture of isomeric acids **8c** (Table 1, entry 5) in MeCN at 65 °C selectively gave the nitrilium zwitterion **30-*m***, which, upon isolation on a SiO_2 column, underwent hydrolysis to the acetamido derivative **31-*m*** (Scheme 4). The latter cluster was hydrolyzed with aqueous



Scheme 4. Synthesis of the 6-ammonium zwitterion **26-*m***.

HCl to the 6-ammonium derivative [*closo*-1-CB_9H_8-COOH-6-NH_3] (**26-*m***), which was isolated in 54% overall yield (Table 4, entry 3). This procedure represents a significant simplification of the preparation of this previously reported amino acid.[14]

Analysis of the data in Tables 2–4 indicates that the iodonium zwitterions react with nucleophiles according to one of three mechanisms: I) addition–reductive elimination via a tricoordinated iodine species (the 10-I-3 intermediate), II) single-electron transfer followed by cleavage of the I–Ar bond in the 9-I-2 intermediate, or III) heterolysis of the I–B bond and formation of a boronium ylide, which is trapped with a nucleophile, as shown for **11a-*p*** in Scheme 5. The first



Scheme 5. Three possible pathways for the reaction of the phenyliodonium zwitterion **11a-*p*** with nucleophiles.

two mechanisms are common for aryl carboranyl[25] and diaryl iodonium salts,[26] whereas the third mechanism is typical for dinitrogen zwitterions.[13]

The addition–reductive elimination mechanism (I) operates at lower temperatures for charged nucleophiles, such as CN^- and AcO^-, which form trigonal-bipyramidal 10-I-3 intermediates (e.g. **32-*p*** in Scheme 5), and for clusters **1–4** is generally highly selective for substitution at the B atom. In the transition state, presumably of tetragonal-pyramidal geometry, the nucleophile migrates to the boron atom and is reductively eliminated, thus relieving the steric strain.[25a]

The reaction of **12** (Ar = $MeOC_6H_4$) with CN^-, however, proceeds differently, presumably by a mechanism involving single-electron transfer (SET) from the cyanide to the iodonium center, followed by homolysis of the I–Ar bond in the 9-I-2 intermediate (II),[25c] as evident from the formation of **28** and the presence of significant amounts of anisole in the reaction mixture. Similarly, the iodonium zwitterion **11a-*p*** undergoes efficient SET from a Grignard reagent to form **29-*p*** exclusively (Table 4 and Scheme 5).

Finally, substitution on the cluster with a weak nucleophile (e.g. MeCN, thian, thioformamide) proceeds presumably through the boronium ylide mechanism (III; for example, **33-*p*** in Scheme 5), which requires higher temperatures and is occasionally complicated by the competing insertion of the ylide into the C–H bond of ArI. Consistent with this mechanism are products of these thermal reactions, for example, the efficient formation of *N*-pyridinium derivatives and ArI. Further support for the involvement of boronium ylides is provided by MP2//DFT calculations, which show generally low ΔG_{298} values for heterolysis of the I–B bond in these zwitterions (e.g. 17.4 kcal mol^{-1} for **11a-*p*** versus 31.4 kcal mol^{-1} for [9-PhI-*m*-$C_2B_{10}H_{11}$]$^+$ in MeCN dielectric medium).[18]

In conclusion, we have demonstrated a simple, convenient, and general two-step method for the practical preparation of a broad spectrum of *closo*-borate derivatives via aryliodonium zwitterions. The presented method provides unprecedented access to functionalized *closo*-borates and new classes of pharmaceuticals and materials, such as liquid crystals, with tailored properties. The presented reactions demonstrate the synthetic versatility of the *closo*-borate aryliodonium zwitterions and suggest their rich chemistry in reactions with other nucleophiles, palladium-catalyzed coupling processes, and photochemistry commonly used with diaryliodonium and arylcarboranyliodonium[25] salts.[26] In this respect, the presented method provides a new and versatile tool for the construction of B–X bonds in *closo*-boranes.[8] We are currently expanding the scope of these reactions, investigating their mechanisms, and exploring them for the preparation of new materials.

Keywords: *closo*-borates · cluster compounds · functionalization · iodonium zwitterions · synthetic methods

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