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Letter

Borenium Ylide-Mediated 12-B Arylation of Carborane Anions

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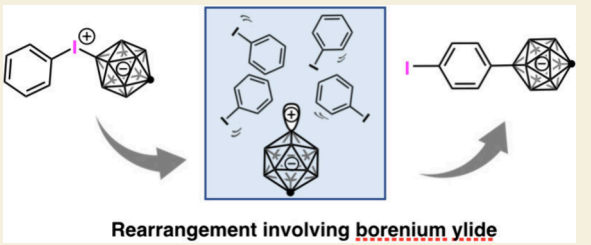
ABSTRACT: Developing novel approaches for B-vertex modification is significant in the chemistry of icosahedral boron clusters. Here, we report a protocol for the transformation of air-stable 12-aryliodonium carborane anions, which are readily accessible on a gram scale from the corresponding (diacetoxyiodo)arenes ($ArI(OAc)_2$) and carborane anion, to 12-aryl-carborane anions. Mechanistic studies support the idea that the 12-B arylation proceeds via intramolecular reductive C−B bond formation on the carborane 12-borenium ylide, followed by rearomatization. The reaction proceeds under mild conditions in air and is suitable for one-pot synthesis without the need for purification of the 12-aryliodonium carborane anions. B−B coupling reaction at the 12-B vertex affords dumbbell-type carborane anion dimers. This reaction offers an alternative approach for B−C bond formation in *closo* borates, complementing conventional cross-coupling approaches.



KEYWORDS: *arylation, borenium ylide, carborane anions, reaction mechanism, coupling reaction*

Monocarba-*closo*-dodecaborate $[closo\text{-}CHB_{11}H_{11}]^-$ (denoted here as "carborane anion"; $CB_{11}H_{12}^-$, **1**) is a highly symmetrical icosahedral anionic cluster molecule that consists of one carbon and 11 boron atoms (Figure 1A).[1] Due to its three-dimensional aromaticity of **1**, its negative charge is delocalized throughout the cage, resulting in good chemical/thermal stability, low nucleophilicity/basicity, and high rigidity.

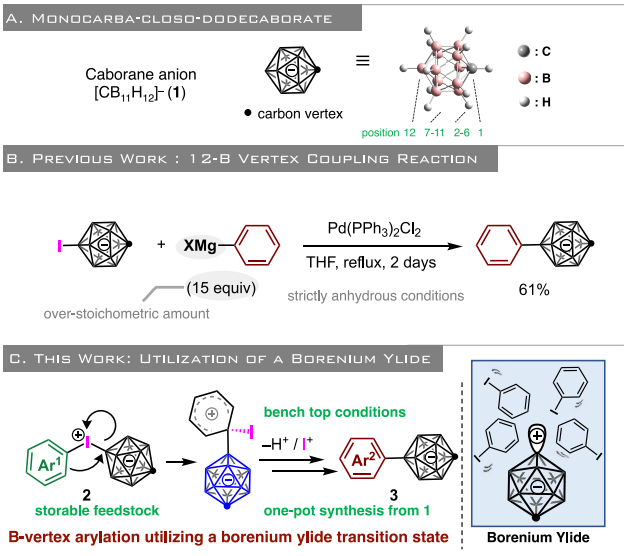


Figure 1. (A) Carborane anion. (B) Previous work on arylation of the B12 vertex. (C) This work.

Consequently, carborane anions are one of the most important scaffolds of weakly coordinating anions (WCAs),[2] and are potentially attractive platforms for creating various functional materials and bioactive/pharmaceutical molecules.[3] Nevertheless, carborane anions have not yet been widely utilized in such applications, largely because the synthetic methodology remains underdeveloped. Historically, functionalization of carborane anions has been limited to simple electrophilic substitution reactions at the boron vertices, such as halogenation and methylation.[1a] In recent years, increasing attention has been devoted to functionalization of carborane anions, but recent advances, including our contributions, have focused on carbon (1-C) vertex modifications.[4] In contrast, synthetic chemistry at the boron vertices of carborane anions remains underdeveloped, even though modifications of the lower hemisphere (7−12-B vertices) are expected to directly improve the physicochemical properties and chemical stability by delocalizing and shielding the negative charge. Intrinsic difficulties include steric hindrance and the unique electronic structure of the carborane anion. For example, no general method is available for metalation reactions at the 12-B vertex of carborane anions, such as halogen-metal exchange, deprotonative metalation, and oxidative metalation. In this context, the palladium-catalyzed cross-coupling of 12-

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iodo-carborane anions with Grignard reagents, enabling the installation of aryl groups at the 12-B position, reported by Michl and co-workers, is noteworthy (Figure 1B).[5]

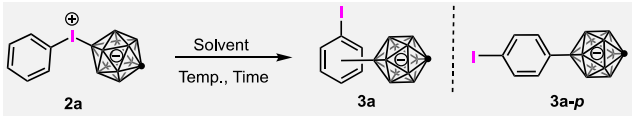
This cross-coupling process represents a significant advancement as a new variant of the Corriu−Kumada−Tamao protocol, but important issues of scalability remain. In particular, the need for a large excess (generally 15 equiv) of aryl Grignard reagents, along with the requirement for strictly anhydrous conditions under an inert atmosphere, has limited its broader application. Regarding the installation of aryl groups on boron vertices at positions 2−6 or 7−11 of carborane anions, this has been achieved through methods involving B−H activation and transition-metal-catalyzed coupling reactions utilizing a directing group.[6] Similar methods for B−aryl formation, employing cross-coupling of halogenated boron clusters, have also been applied in the case of dodecaborate $[B_{12}H_{12}]$.[2−7]

Alternative strategies involve the use of boron-centered cations, such as borenium and boronium cations, which are highly electrophilic and can facilitate unique transformations at boron sites. Kaszyński and co-workers developed 12-aryliodonium carborane anions as intermediates for nucleophilic substitution at the 12-B vertex, expanding the functionalization scope of carborane anions.[9] However, direct arylation through these approaches remains challenging due to the limited reactivity of aryl nucleophiles. Similarly, Grushin and co-workers pioneered the utilization of B−iodonium derivatives of carborane $[C_2B_{10}H_{10}]$, achieving nucleophilic substitution at the boron atom, albeit they did not propose the generation of boronium cation.[3h,8] Xie and co-workers introduced a diazonium salt-based approach that generates boronium-like intermediates in carborane clusters, enabling selective boron substitution reactions.[10] Other studies have also shown that cationic boron sites in cage-opened clusters can participate in electrophilic substitution reactions. Hawthorne and co-workers demonstrated that acid-induced opening of the $[B_{10}H_{10}]^{2-}$ cluster generates an electrophilic boron cation intermediate capable of selective C−H activation of arenes, leading to functionalized boron clusters.[11] Building on this, Spokoyny and co-workers utilized these cage-opened boron cations for the electrophilic borylation of arenes.[12] Moreover, Duttwyler and co-workers investigated metal-stabilized borenium cations within carborane anion frameworks, demonstrating that transition metal coordination can stabilize reactive borenium species.[13]

Here, we report a reaction on the carborane anion 12-B vertex which opens up an alternative approach to the 12-B arylation of carborane anions **3** (Figure 1C). This reaction involves a borenium ylide as a transition state in intramolecular reductive C−B bond formation and proceeds under mild, metal-free conditions. It should be noted that Sivaev and co-workers proposed the generation of borenium cations from iodonium derivatives of cobalt bis(dicarbollide) anions (COSAN), enabling electrophilic activation of arenes to produce arylated COSAN.[14] Furthermore, Michl and co-workers proposed the formation of a borenium ylide intermediate [12-dehydro-1-$(C_6H_{12}O_2)$B-$CB_{11}Me_{10}$] during the thermal reaction of the lithium salt of permethylated carborane anion [1-$(C_6H_{12}O_2)$B-$CB_{11}Me_{11}]^-$ in benzene at 190 °C, resulting in subsequent arylation.[4g] This process was thought to involve the abstraction of a methyl group at the 12-B vertex by a lithium cation, leading to the generation of the ylide. However, the requirement of high temperatures and specific methylated substrates limits the practical applicability of this method.

These reports inspired us to explore similar transformations, leading to our serendipitous discovery of this unique rearrangement reaction during our studies on thermal solvolysis of aryl iodonium carborane anions **2**. Iodonium anions **2** are readily available on a gram scale in a single step without the need for purification by column chromatography, and they are bench-storable and easy to handle, thus providing an excellent synthetic platform for generating 12-aryl-carborane anions. Building upon the work of Kaszyński and co-workers on utilizing the potent leaving-group ability of 12-phenyliodonium carborane anion **2a** for nucleophilic substitution at the 12-B vertex,[8,15] we explored its application for the preparation of 12-OH−$CB_{11}H_{11}^-$ (which is unavailable by traditional carborane anion electrophilic substitution protocols)[16] by means of thermal solvolysis of **2a** in hot water, we occasionally found that small amounts of 12-B arylated products were formed, as detected by ESI-MS. Gratifyingly, we found here that heating **2a** in H_2O at 100 °C for 2 days afforded **3a** in a good yield, though as a regioisomeric mixture. In contrast, no arylation products at all were obtained at 40 °C (Table 1, runs 1 and 2).[15,17,18] We considered that this

Table 1. Solvolysis of 12-Phenyliodonium Carborane Anion 2a[a]



Run	Solvent	Temp. (°C)	Time (day)	Product(s) [Yield (%)[b]]
1	H_2O	100	2	**3a**[c]
2	H_2O	40	2	–[d]
3	CH_3OH	40	2	**3a**[c]
4	Toluene	40	2	**3a**[c]
5	CH_3CN	40	2	–[d]
6	CH_3CN	80	1	–[e]
7	DIPEA	40	2	**3a-*p*** [74]
8	DIPEA	40	1	**3a-*p*** [68]
9[f]	DIPEA	40	1	**3a-*p*** [76]

[a]Run on 0.40 mmol (0.15 M) scale. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. [c]Complex reaction mixtures with a large number of unidentified signals according to ^{1}H NMR. [d]Almost all of the starting material (**2a**) was recovered. [e]Ritter-type product nitrilium inner salt **I** (38%) was obtained (see Figure 3 for details). DIPEA = *N*,*N*-diisopropylethylamine. [f]Reaction conducted under microwave irradiation.

peculiar arylation at the 12-B vertex probably proceeds via intramolecular reductive C−B bond formation of **2a**, and this idea was supported by our model calculations (Figure 2): (1) the initial C−B bond formation at the *ipso* position of iodobenzene is a critical step and requires a reasonable activation energy of 18.1 kcal/mol to give a *σ*-complex **INT2-*i***, (2) then successive rearrangements on the carborane 12-borenium ylide[19,20] take place with very small activation barriers. However, it should be noted that we could not accurately calculate the activation energy of the deprotonation step, making it difficult to definitively identify which step is rate-determining. Our present calculations suggest that the initial C−B bond formation likely plays a central role, while rearomatization also appears crucial. Examination of several solvents showed *N*,*N*-diisopropylethylamine (DIPEA) to be greatly superior to H_2O, methanol, toluene, or acetonitrile (Table 1). When **2a** was stirred in DIPEA at 40 °C for 2 days or 1 day, the *para*-isomer **3a-*p*** was obtained

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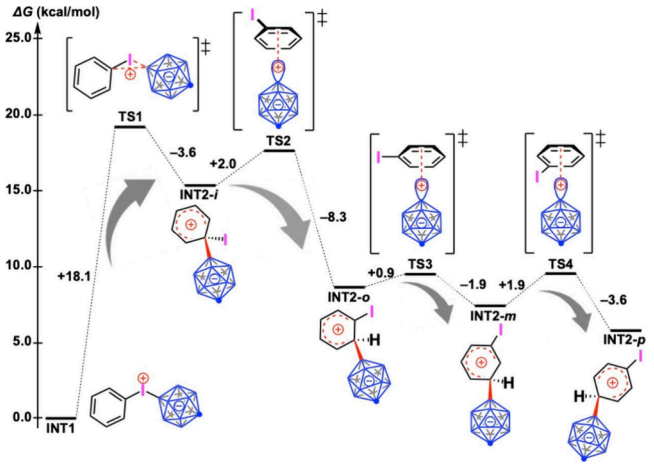


Figure 2. DFT calculation of intramolecular rearrangement reaction at the M06/lanl2dz level (for I) & 6-31+G** level (others) (ΔG in kcal/mol).

as the sole product in 74% or 68% yield, respectively (runs 7 and 8). Microwave-assisted heating enabled faster synthesis (run 9). These observations are in good accordance with our model calculations, suggesting that the solvent should exhibit suitable polarity to stabilize the highly polarized **TS**s/**INT**s as well as appropriate basicity for smooth deprotonative rearomatization. We speculate that DIPEA facilitate the deprotonation of the most thermodynamically stable intermediate, **INT2**-*p*, leading to the selective formation of **3a**-*p*. In contrast, solvents with lower basicity than DIPEA, such as methanol, toluene, or water, the C−B bond formation and rearomatization steps could not proceed efficiently, resulting in more complex reaction mixtures and lower selectivity. It is interesting to note that the nitrilium salt **I** was obtained in 38% yield in the thermal solvolysis of **2a** at 80 °C in acetonitrile (Table 1 run 6, and Figure 3).[21] This

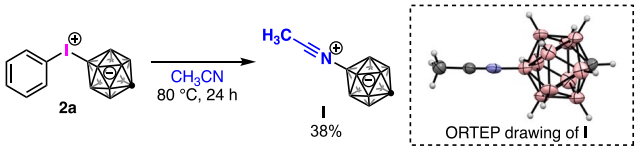
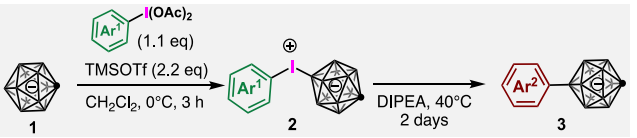


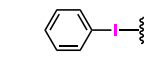
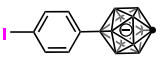
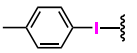
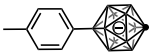
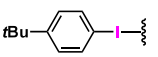
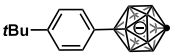
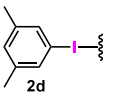
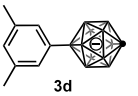
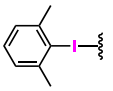
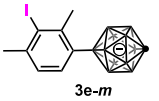
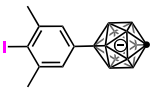
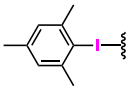
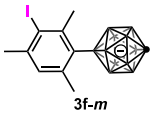
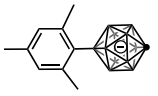
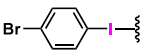
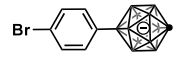
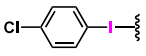
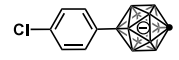
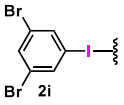
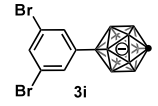
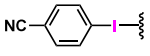
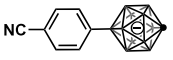
Figure 3. Thermal decomposition of **2a** in MeCN (Table 1 Run 6).

observation strongly suggests that the 12-borenium ylide shows pronounced electrophilicity, confirming the key role of the balance between basicity and nucleophilicity of the solvent in this reaction.

Inspired by these observations, we became interested in exploring synthetic applications of this rearrangement reaction to the 12-B arylation of carborane anions. Particular synthetic advantage is afforded by the ready availability of the precursor iodonium compounds. Kaszyński et al. reported a simple one-step synthesis of **2a** by the treatment of **1** with $PhI(OAc)_2$ in aqueous acetic acid at 0 °C.[8a] However, it was found that this protocol often yields a mixture of 12- and 7-aryliodonium products. Thus, we first proceeded to optimize the reaction conditions for the preparation of 12-aryliodonium carborane anions **2**. After considerable experimentation, we developed a TMSOTf-mediated selective 12-B−I bond formation reaction of **1** with $PhI(OAc)_2$ in dichloromethane (DCM) (Table 2): this reaction chemo-/regioselectively converts a range of aryl

Table 2. Synthesis of Carboranyl Aryl Iodonium and Intramolecular Arylation Reaction at the B12 Vertices



Run	2		3	
	Ar^1	Yield (%)[a]	Structure	Yield (%)[b]
1	 **2a**	60	 **3a-*p***	80
2	 **2b**	69	 **3b**	90
3	 **2c**	72	 **3c**	89
4	 **2d**	61	 **3d**	71
5	 **2e**	63	 **3e-*m***	49
			 **3e-*p***	48
6	 **2f**	82	 **3f-*m***	74
			 **3f-*i***	22
7	 **2g**	68	 **3g**	65
8	 **2h**	64	 **3h**	67
9	 **2i**	75	 **3i**	63
10	 **2j**	64	 **3j**	—[c]

[a]Isolated yield. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. [c]Complex reaction mixtures with a large number of unidentified signals in ^{1}H NMR were obtained.

iodides, including multiply alkylated/halogenated/sterically hindered ones, into the corresponding 12-aryliodonium carborane anions **2** in modest to good yields.

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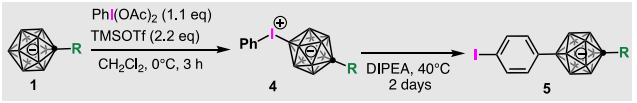
With the various iodonium precursors in hand, we next explored the scope of the thermal rearrangement reaction of **2** (Table 2). Under the optimized conditions (Table 1 run 7), variously functionalized aryliodonium compounds **2a**−**2i** smoothly underwent the desired reductive 12-B−C bond formation. Interestingly, the deiodo-aromatization process proceeds preferentially to give cross-coupling products in moderate to high yields (runs 2−4, 7−9) probably because electron-donating *p*-alkyl/halogen and *m*,*m*-dimethyl/dibromo substituents on the iodobenzene ring can effectively stabilize **INT2**-*i* through a resonance effect. Sterically hindered *o*-xylene and mesitylene were also employed, but in these cases, due to steric hindrance, the reaction proceeded via alternative pathways leading to mixtures of regioisomers: iodonium **2e** gave **3e**-*m* and **3e**-*p* in a 1:1 ratio in 97% total yield (run 5), whereas **2f** afforded a 1:3 mixture of **3f**-*i* and **3f**-*m* in 96% total yield (run 6).[22] These results suggest that *o*,*o*-disubstitution destabilizes *ipso* σ-complex (**INT2**-*i*) formation due to steric hindrance, and thus the subsequent rearrangement proceeded smoothly to give the *meta* σ-complex **INT2**-*m* stabilized by *o*-/*p*-methyl groups, leading to the formation of 12-(*m*-IC_6H_4)-$CB_{11}H_{11}^-$ **3f**-*m* by deprotonative aromatization. Attempts to extend the substrate scope to iodobenzene derivatives with strongly electron-withdrawing groups, such as nitroiodobenzenes, iodopyridines, iodothiophenes, and perfluoro-substituted iodobenzenes, were unsuccessful; the desired carboranyl iodonium precursors could not be obtained under our reaction conditions. We speculate that electron-deficient benzene rings (bearing electron-withdrawing groups) are less effective at stabilizing the cationic iodine center in the iodonium precursors. This lack of stabilization may lead to instability and rapid decomposition of the precursor. In the case of *p*-cyano iodobenzene, we were able to synthesize the precursor **2j**; however, the subsequent arylation did not proceed selectively, and the desired products were not formed (entry 10). We postulate that efficient coordination from the benzene ring to the borenium ion is crucial for the reaction to proceed. We also investigated the applicability of this methodology to a range of C-vertex functionalized carborane anions, including methylated (**4a**)/silylated (**4b**)/carbonylated (**4c**)/iodinated (**4d**) ones (Table 3). The synthesis of various iodonium precursors and the subsequent rearrangement proceeded smoothly, selectively yielding the *para*-isomers without affecting the 1-*C*-functional groups (runs 1−4).

Further applications of this methodology are illustrated in Figure 4. We first demonstrated the one-pot 12-*B*-arylation of the carborane anion **1** (Figure 4A): starting with (1) the preparation of iodonium compound **2a**, followed by (2) solvent exchange from dichloromethane to DIPEA, and (3) heating/stirring at 40 °C for 2 days in one pot to afford the desired product **3a** in comparable yield to that of the two-pot procedure (Table 2 run 1). The present reactions can afford 12-arylcarborane anions containing C−I/C-halogen bond(s) on the aromatic ring, which are amenable to further functionalization, providing a basic architecture for functional materials chemistry. For example, the Suzuki−Miyaura cross-coupling reaction converted **3a**-*p* to the biphenyl-substituted carborane anion **5** in 78% yield (Figure 4B). Considering that a unique electronic interaction (extended electron delocalization) between σ- and π-aromaticity has been identified in the 1-*C*-arylated carborane anion,[4k] the σ−π conjugation of in 12-*B*-arylated carborane anions is of interest. Finally, we examined whether this methodology is also applicable to the dicarboranyliodonium salt protocol for the preparation of a new family of carborane anion dimers.,[4i,23] After extensive experimentation, we found that stirring **6** in 1,3-dimethyl-2-imidazolidinone (DMI) at 120 °C gave a 1:2 mixture of 7-*o* and 7-*m* in 51% yield (Figure 4C). Carborane anion **1** and 12-iodo-carborane anion were detected by ESI-MS, indicating that the decomposition of **7** might be the reason for moderate yield observed in this reaction. DIPEA did not work well in this reaction. The regioisomers could be separated by column chromatography. Single-crystal X-ray diffraction analysis unambiguously established the dimer structures of 7-*o* and 7-*m*, in which the two boron vertices of the carborane anion units are directly connected. Since B-metal species are difficult to prepare at carborane anion vertices, B−B couplings of B vertices between carborane anions are usually inaccessible. Microwave-assisted heating markedly shortened the reaction time, demonstrating the potential for faster synthesis. To shed light on the reaction mechanism, DFT calculations were performed (Figure 4D). The dicarboranyliodonium salt (**INT3**) undergoes the rearrangement reaction (via **TS5**) in a similar manner to the S_N1-type nucleophilic aromatic substitutions often found in the case of aryldiazonium salts to yield **INT4**-*m*. **TS5** contains an intrinsically unstable 12-borenium cation moiety (carborane 12-borenium ylide), stabilized in part by the B−I and B−H bonds of another carborane molecule, and hence is 28.5 kcal/mol higher in energy than **INT3**. **INT4**-*m* is a 3c-2e bonding complex that can either form a B−B bond by deprotonation reaction with a base to yield a coupling product 7-*m* or undergo further rearrangement via a boronium cation (nonclassical boryl cation) **TS6** partially stabilized by two B−H bonds with an overall energy loss of 27.4 kcal/mol, affording **INT4**-*o*.[24] Although the mechanism of the deprotonation in the present cases is not yet clear, the combination of CaH_2 and DMI gave the best result. We speculate that nitrogen atom in DMI might act as a base for the deprotonation of the sterically congested 3c-2e B−H−B bond surrounded with bulky carborane cages. Note

Table 3. Synthesis of Carboranyl Aryl Iodonium and Intramolecular Arylation Reaction with Carbon Vertex Substituents



Run	4		5	
	R	Yield (%)[a]	Structure	Yield (%)[b]
1	Me— **4a**	92	**5a**	75
2	Me_3Si— **4b**	93	**5b**	72
3	Ph **4c**	89	**5c**	76
4	I— **4d**	91	**5d**	79

[a]Isolated yield. [b]Determined by ^1H NMR using mesitylene as an internal standard.

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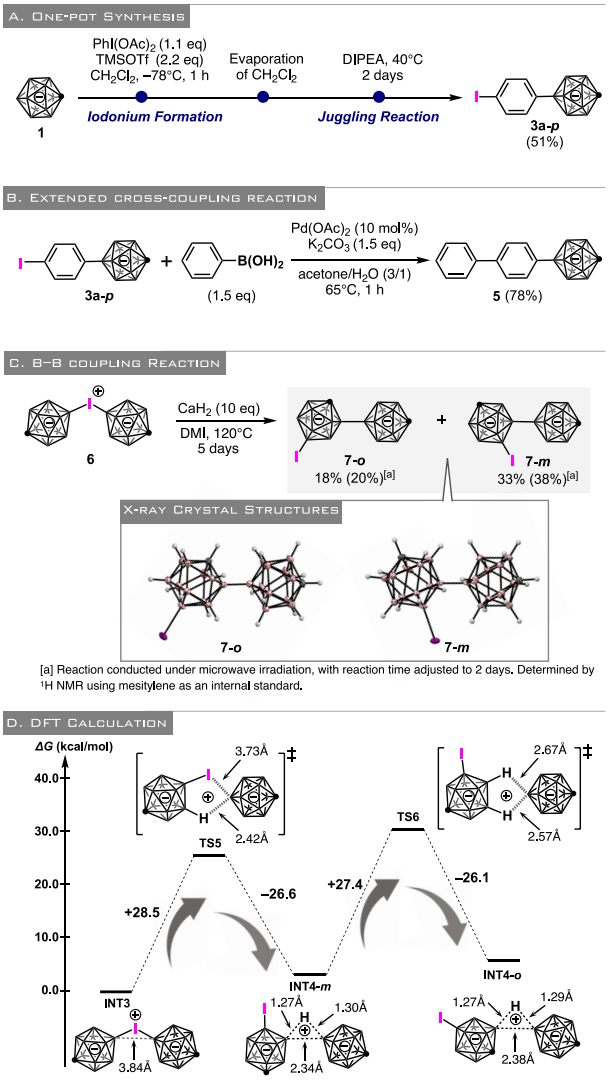

Figure 4. (A) One-pot synthesis. NMR yields. (B) Extended cross-coupling reaction. NMR yields. (C) B–B coupling reaction. Isolated yields. ORTEP drawing of (a) 7-*o* and (b) 7-*m* with thermal ellipsoids at the 50% probability level. Counter cation (PPh_4^+) was omitted for clarity. (D) DFT calculation of intramolecular rearrangement reaction at the M06/6-31+G** level and lanl2dz level (for I) (ΔG in kcal/mol). DMI = 1,3-dimethyl-2-imidazolidinone.

that in the absence of CaH_2, an insoluble gel was obtained, probably owing to polymerization reaction involving DMI.

In conclusion, we present a novel reaction on the carborane 12-B vertex, opening up a new access to diverse 12-B-aryl carborane anions. This reaction involves a borenium ylide in transition state, offering an alternative approach for B–C bond formation in *closo* borates, compared with conventional cross-coupling approaches. It is the first example of an efficient one-pot introduction of aromatics into carborane anions under mild conditions in air. It is applicable to one-pot synthesis without the need for purification of the 12-aryliodonium carborane anions. Notably, an unprecedented B–B coupling at the 12-B vertex afforded dumbbell-type carborane anion dimers. Further work is in progress to expand the scope of this methodology, as well as to study applications of the σ/π-conjugated products and dumbbell-type carborane anions to create functional molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.4c00854.

Experimental procedures, characterization data, computational details (PDF)

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■ DEDICATION

This paper is dedicated to the memory of Professor Josef Michl, a great leader who has explored the fascinating chemistry of

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boron clusters. His groundbreaking work has paved the way for significant advances in this field, inspiring generations of researchers.

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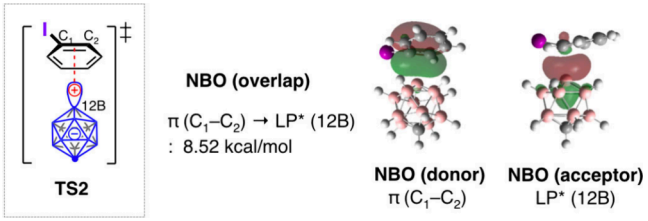

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