Carborate Anions

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Copper-Mediated C–C Cross-Coupling Reaction of Monocarba-*closo*-dodecaborate Anion for the Synthesis of Functional Molecules**

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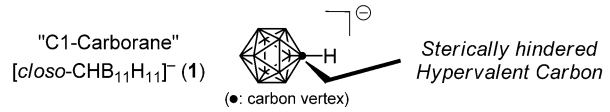
Monocarba-*closo*-dodecaborate $[closo\text{-}CHB_{11}H_{11}]^-$ (**1**; denoted here as "C1-carborane"; Scheme 1) belongs to a class of highly symmetrical cage compounds that exhibit three-dimensional aromaticity, and has exceptional stability, low nucleophilicity/basicity, and high rigidity.[1] For these reasons, C1-carborane has attracted considerable attention as



Scheme 1. C1-carborane (**1**).

a counterion for the isolation of reactive cations,[2] and for activation of catalysts in organic synthesis.[3] Its unique electronic and molecular structures render **1** as an attractive starting material for the construction of various functional molecules[4,5] and bioactive/pharmaceutical building blocks.[6] However, progress in the synthesis of such materials is hindered by the lack of methods for the functionalization of **1**.[7] In particular, no efficient general methods are available for introduction of aryl and sp^2/sp-hybridized carbon centers at the carbon vertex of C1-carborane.[8] A cross-coupling reaction is an obvious method for the introduction of aryl groups and sp^2/sp-hybridized carbon centers at the carbon vertex of C1-carborane derivatives, but has not yet been successful.[1a,9,10] The intrinsic difficulty appears to be associated mainly with the sterically hindered and hypervalent nature of the vertex carbon atom in **1**. We report herein a general and efficient copper-mediated C–C cross-coupling reaction of **1** under palladium catalysis that yields a variety of C-functionalized C1-carborane derivatives and provides a basic architecture for pharmacophores and functional materials. The reaction is demonstrated not only for the parent C1-carborane but also its B-halogenated derivatives. To demonstrate utility of the method and the resulting new class of compounds, we describe the synthesis of multivalent anions and disclose preliminary results of the biological activity and liquid crystal behavior of selected derivatives.

We commenced our studies by screening for a suitable metal species at the C1-carborane carbon vertex for cross-coupling reaction with aryl iodide **2a** under palladium catalysis (Table 1). Reactions of various zinc carborate derivatives **1a** (i.e. Negishi-type reaction),[10] including zincate complexes,[11] were unsuccessful (Table 1, entry 1). The Suzuki–Miyaura-type cross-coupling with pinacol borate **1b** was also examined under a variety of conditions, but failed to give the desired product, affording only halogenated C1-carboranes, with most of the pinacol borate moiety remaining intact (Table 1, entry 2).[12] These results imply that the nature of the vertex carbon atom with respect to transmetalation is quite different from that of typical aryl or alkyl carbon atoms. After extensive screening of other systems, we found that a combination of copper(I) carborate **1c**[13] and a palladium catalyst promoted the coupling reaction with **2a** at room temperature to give the desired product **3a** (Table 1,

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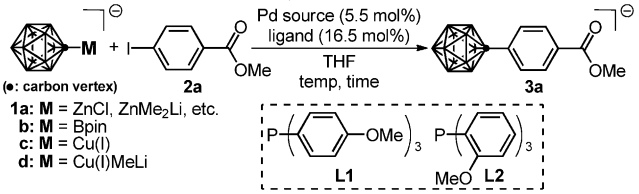
Table 1: Optimization of C–C cross-coupling reaction between C-metalated C1-carborane anion and aryl iodide **2a**.



Entry	**1**	Pd source	Ligand	*T* [°C]	*t* [h]	Yield [%][a]
1	**1a**	various conditions				0
2	**1b**					0[b]
3	**1c**	$[Pd(dba)_2]$	PPh_3	RT	3	52
4	**1c**	$[PdCl_2(PhCN)_2]$	PPh_3	RT	3	47
5	**1c**	$Pd(OAc)_2$	PPh_3	RT	3	57
6	**1c**	$Pd(OAc)_2$	PCy_3	RT	3	51
7	**1c**	$Pd(OAc)_2$	Xantphos	RT	3	67
8	**1c**	$Pd(OAc)_2$	**L1**	RT	3	63
9	**1c**	$Pd(OAc)_2$	**L2**	RT	3	72
10	**1c**	–	**L2**	RT	3	0
11	**1d**	$Pd(OAc)_2$	**L2**	RT	3	0

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The counter cations were not identified. [b] Halogenated carborane derivatives were obtained.

entry 3).[14] The structure of **3a** was confirmed by ^{1}H, ^{1}H{^{11}B}, ^{13}C, and ^{11}B NMR spectroscopy, ESI-MS, X-ray crystallography (Figure 1), and elemental analysis. Among the palladium sources examined, $Pd(OAc)_2$ gave the best results

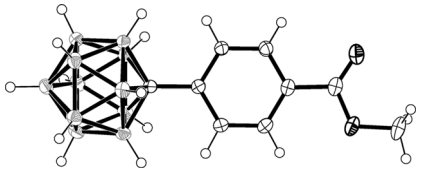
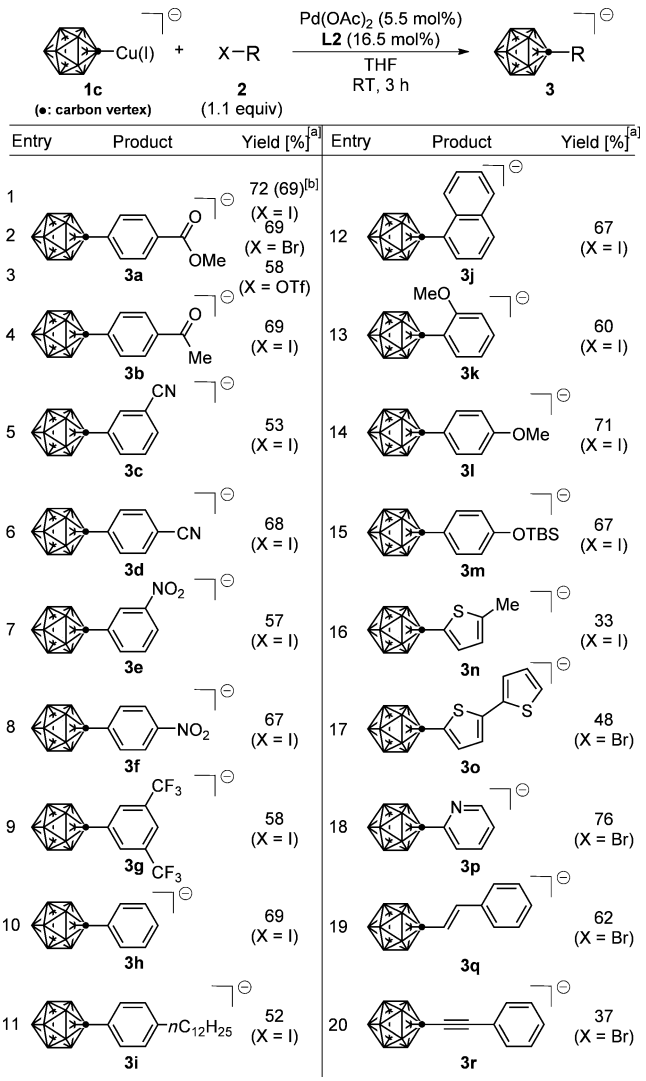


Figure 1. ORTEP drawing of **3a** (ellipsoids set at 50% probability). The tetraphenylphosphonium counterion is omitted for clarity. Boron = gray ellipsoids, carbon = white ellipsoids.

Table 2: Scope of palladium-catalyzed copper-mediated cross-coupling reaction of C1-carborane anion derivatives.



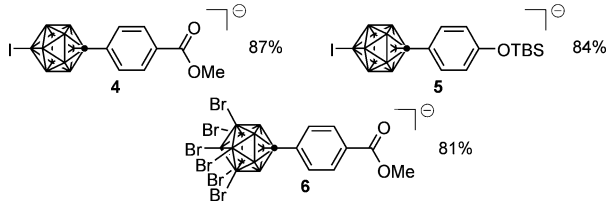
[a] Determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [b] Yield of the isolated cesium salt.

(Table 1, entries 3–5). While the effects of phosphine ligand structures were unremarkable, the use of tris(*o*-methoxyphenyl)phosphine (**L2**) improved the reaction efficiency, to give **3a** in 72% yield (Table 1, entry 9).[15] The reaction did not proceed at all in the absence of palladium (Table 1, entry 10).[16] The use of methylcuprate analogue **1d** resulted in no product formation (Table 1, entry 11). Under the optimized conditions no side reactions of the C1-carborane were observed and the reported yields reflect incomplete transformations of **1**.

With the optimized reaction conditions established, the scope of this coupling reaction was examined, and representative results are summarized in Table 2. As well as aryl iodides, aryl bromides and triflates can be used in this reaction (Table 2, entries 1–3). Electron-withdrawing groups, such as COOMe, NO_2, CN, and CF_3, which are sensitive to metal reagents, are compatible with the cross-coupling reaction conditions (Table 2, entries 1–9). The reaction with iodobenzene proceeded in a good yield of 69% (Table 2, entry 10). Coupling with an aryl group having a long alkyl chain gave an oily ion-pair product after counter ion exchange to PPh_4^+ (entry 11).[12] Sterically demanding iodides, *ortho*-iodoanisole and 1-iodonaphthalene, also gave good yields of C1-arylated products (Table 2, entries 12 and 13). In addition, iodobenzenes with electron-donating methoxy substituents also underwent efficient coupling reaction (Table 2, entries 13 and 14). The base-sensitive phenolic silyloxy group was tolerated under these reaction conditions (Table 2, entry 15). The reaction allows the efficient installation of heterocyclic groups, such as thienyl and pyridinyl at the C1 vertex (Table 2, entries 16–18). Moreover, the reaction conditions were applicable to alkenyl and alkynyl substrates (Table 2, entries 19 and 20). To our knowledge, this is the first general method for the C–C cross-coupling of C1-carborane for the incorporation

of a wide range of aryl and other sp^2/sp-hybridized carbon centers at the carbon vertex.

Given the importance of incorporation of the C1-carborane anion into a variety of functional molecules, the C–C cross-coupling reactions of substituted carborate anions were investigated. The introduction of aryl groups to the carbon vertex of the 12-iodo derivative [*closo*-1-$CB_{11}H_{11}$-12-I]$^-$ was achieved under the present reaction conditions, and C-arylated compounds **4** and **5** were prepared in 87 and 84% yield, respectively, as determined by NMR spectroscopy (Scheme 2). The use of hexabromocarborate anion afforded

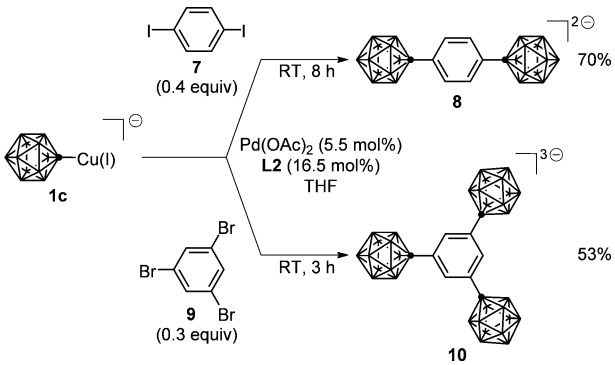


Scheme 2. Cross-coupling reaction with substituted C1-carborate anions.

the desired coupling product **6** in 81% yield. Thus, halogen atoms on the boron vertices were well tolerated under the reaction conditions, which enables synthetic access to more complex functionalized molecules that possess the C1-carborane as part of the core (see below).

The scope of the cross-coupling reaction was extended to multiple cross-coupling of C1-carborane to polyhaloarenes to provide densely functionalized polyanionic derivatives (Scheme 3 and Figure 2). Thus, when *p*-diiodobenzene (**7**) was treated with 2.5 equivalents of **1c** under the optimized reaction conditions, the desired compound **8**, having two C1-carborane anionic moieties, was obtained in 70% yield. From the reaction of 1,3,5-tribromobenzene (**9**), the trianion **10** was the sole isolated product, the cesium salt of which was soluble in both ethyl acetate and water. Thus, the present cross-coupling reaction can be used to create/control the hydrophobic/hydrophilic properties of molecules, and is expected to provide new tools for developing pharmacophores and use in medicinal chemistry.

We examined the potential value of the functionalized C1-carborane obtained in this work to generate biologically



Scheme 3. Multiple cross-coupling reactions.

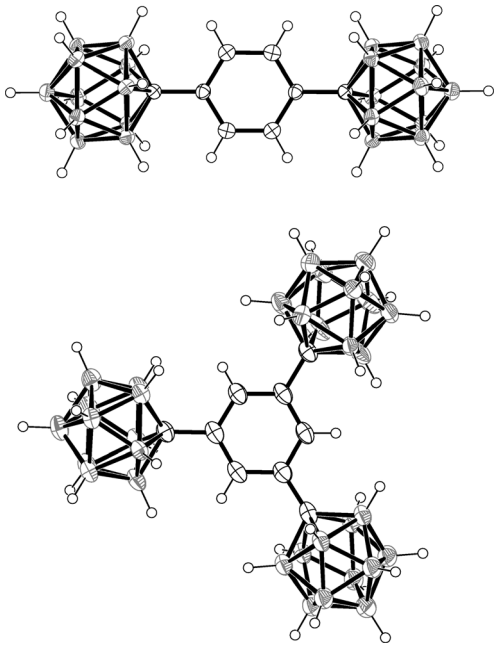


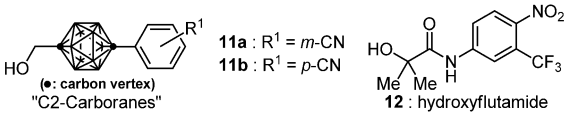
Figure 2. ORTEP drawing of **8** (top) and **10** (bottom) (ellipsoids set at 50% probability). The tetraphenylphosphonium couterions are omitted for clarity.

active molecules. It has previously been reported that (neutral) dicarba-*closo*-dodecaborane (so-called C2-carborane) derivatives having a cyanophenyl group (e.g. **11a** and **11b**) exhibited nuclear androgen receptor (AR) modulating potency.[17] In a competitive binding assay using human AR, and ^{3}H-labeled natural hormone dihydrotestosterone (DHT),[18] compounds **3c** and **3d** inhibited the specific binding of [^{3}H]DHT with AR at micromolar concentrations, comparable to those of C2-carborane derivatives **11a** and **11b** and hydroxyflutamide (**12**; Table 3). These compounds also inhibited DHT-induced cell growth of androgen-dependent SC-3 cells.[19] These results suggest that the new compounds could function as AR modulators, and further investigations on the inhibitory mechanism are in progress.

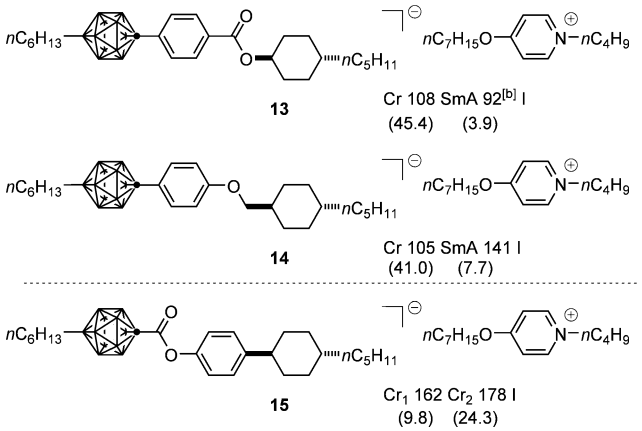
Table 3: Biological activities of arylated C1-carborane anions and C2-carboranes toward AR.

Compound	Binding IC_{50} [M][a]	SC-3 Cell growth inhibition [%][b]
3c	4.75×10^{-6}	36
3d	3.79×10^{-6}	79
11a	8.86×10^{-7}	93
11b	4.99×10^{-6}	81
12[c]	7.20×10^{-6}	92

[a] IC_{50} values for specific binding of [^{3}H]DHT to human androgen receptor ligand-binding domain. The concentration of [^{3}H]DHT was 4.0×10^{-9} M. [b] Inhibition of SC-3 cell proliferation induced by 1.0×10^{-9} M DHT. The concentration of the compounds (**3c**, **3d**, **11a**, and **11b**) was 1.0×10^{-5} M. [c] AR antagonist hydroxyflutamide (**12**) was used as the positive control.[17]



Finally, two ionic liquid crystals (ILCs) based on the C-arylated C1-carborate anions have been prepared (Scheme 4). Mesogenic behavior of such compounds is anion driven and such materials are of general interest for applications in lithium-ion batteries and dye-sensitized solar



Scheme 4. Transition temperatures [°C][a] and enthalpies [kJ mol^{-1}] (in parentheses) for the ionic liquid crystals based on the C-arylated carborate anions. [a] Transition temperatures obtained on heating. [b] Monotropic transition temperature obtained on cooling. Cr = crystalline, I = isotropic, SmA = Smectic A phase.

cells. Thus, pyridinium salts **13** and **14** were synthesized from **4** and **5** by alkylation at the B(12) vertex by a Negishi-type cross-coupling.[4a,12] Noteworthy, ion pair **13**, with the C-aryl junction, melted at 108 °C and formed a monotropic SmA phase, whereas isomeric ion pair **15**, with the COO group in a different position, had a significantly higher melting point and did not show mesogenic behavior.[4a] Furthermore, **14**, having an oxymethylene linker, exhibited an enantiotropic SmA phase with a wide mesophase range (36 K). These results clearly indicate that the structure of the anions impacts mesogenic properties. More detailed investigation of ILCs based on C-arylated derivatives will be reported separately.

In summary, we have developed a C–C cross-coupling reaction of monocarba-*closo*-dodecaborate (C1-carborane) and its derivatives. Our method enables the efficient introduction of a broad range of (hetero)aryl groups and other sp^2- and sp-hybridized carbon centers for the first time. As an application of the reaction, we describe the synthesis of multivalent anionic molecules by a multiple coupling process. Arylated C1-carboranes have AR-modulatory activity, and thus show potential as biological tools/pharmacophores. The high potential of this method in the synthesis of functional materials was further illustrated by the preparation of new ILCs with favorable mesogenic properties. From the perspective of reaction development, we believe that this work also further underlines the utility of copper(I) species as a transmetalating partner in cross-coupling reactions of sterically hindered carbon centers. Further mechanistic investigations, for example, on the specific role of copper reagents in the transmetalation step, and into the incorporation of C1-carborane anion moieties to create functional molecules with unique properties, are the subjects of ongoing research.

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Keywords: carborate anion · copper-mediated cross-coupling · ionic liquid crystals · multivalent anions · pharmacophores

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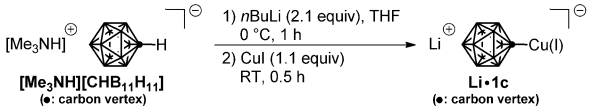
[12] For details, see the Supporting Information.

[13] **1c** was readily prepared in situ according to the following scheme and was used directly for the coupling reaction. Although the structure of **1c** is drawn here simply as a [(carboranyl)Cu]$^-$ species, it would have the aggregated form (i.e. [(carboranyl)Cu]$_n^{n-}$), or be coordinated by a Lewis base such as THF (i.e. [(carboranyl)Cu(thf)]$^-$). We thank one of the referees for these suggestions.



[Me$_3$NH][CHB$_{11}$H$_{11}$] (•: carbon vertex) — Li•1c (•: carbon vertex)

[14] In the case of dicarba-*closo*-dodecaborane (C2-carborane), a similar palladium-catalyzed coupling reaction was reported, see: a) U. Schöberl, T. F. Magnera, R. M. Harrison, F. Fleischer, J. L. Pflug, P. F. H. Schwab, X. Meng, D. Lipiak, B. C. Noll, V. S. Allured, T. Rudalevige, S. Lee, J. Michl, *J. Am. Chem. Soc.* **1997**, *119*, 3907; b) A. M. Spokoyny, O. K. Farha, K. L. Mulfort, J. T. Hupp, C. A. Mirkin, *Inorg. Chim. Acta* **2010**, *364*, 266. See also Ref. [16].

[15] **3a** was isolated as a cesium salt (Cs·**3a**) in 69% yield for entry 1 in Table 2. For details, see the Supporting Information.

[16] In contrast, (dicarba-*closo*-dodecaboranyl)copper(I) species react with aryl iodides in the absence of palladium catalyst. This reaction has been widely utilized for the arylation of (neutral) C2-carborane species. See: R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride, K. Wade, *J. Organomet. Chem.* **1993**, *462*, 19.

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