

Exhaustive Cyanation of the Dodecaborate Dianion: Synthesis, Characterization, and X-ray Crystal Structure of $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ Austin A. Kamin and Marcus A. Juhasz*[✉]

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Supporting Information

ABSTRACT: The percyanated dodecaborate anion $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ was prepared by reacting $[\text{B}_{12}\text{I}_{12}]^{2-}$ with CuCN in the presence of a palladium catalyst at elevated pressure and temperature in a microwave reactor. The fully cyanated cluster was isolated as a tetraethylammonium salt in yields of up to 39% and characterized by NMR and IR spectroscopy and mass spectrometry. The crystal structure of a copper complex of the percyanated anion, $(\text{CH}_3\text{CN})_3\text{Cu}[\mu\text{-B}_{12}(\text{CN})_{12}]\text{Cu}(\text{NCCH}_3)_3$, was determined by single-crystal X-ray diffraction.

The *closo*-dodecaborate ion (**1**, i.e., *closo*- $[\text{B}_{12}\text{H}_{12}]^{2-}$) has held a prominent place in chemistry since the first prediction of its stability¹ and its subsequent synthesis.² Today this cluster appears in introductory inorganic chemistry textbooks and is familiar to chemists across specialties as an example of a perfectly icosahedral molecule. The exceptional stability of the boron skeleton in **1** and its derivatives is noteworthy. In striking contrast to highly reactive small boron hydrides (e.g., diborane, a notoriously pyrophoric species), salts of **1** are among the most stable molecules known to chemists; this anion survives extended heating in strongly acidic or alkaline solutions, and its cesium salt withstands heating in excess of 800 °C.³ A variety of potential applications have been proposed for derivatives of **1**. These include uses as drugs or imaging agents in medicine,⁴ as electrolytes for lithium- and magnesium-ion batteries,^{5–10} as weakly coordinating anions (WCAs) for use in catalysis,^{11,12} and in the preparation of superacids.^{13,14}

The derivatization of polyhedral boron clusters is an established strategy for tuning their properties for specific applications.^{9,15,16} A variety of methods for modifying **1** have been described.¹⁷ Some reactions of **1** are analogous to those for derivatizing organic aromatic molecules: for example, BH vertices can be halogenated by electrophilic substitution,^{11,18} and BI vertices are known to undergo cross-coupling reactions.^{19,20} Functionalization of **1** at multiple vertices is possible, and synthetic routes to perfunctionalized derivatives have been the subject of a recent review.²¹ Examples of uniformly perfunctionalized derivatives of **1** are limited: permethylated, perhalogenated, and perhydroxylated derivatives can be synthesized directly from **1**, and ester, carbamate, carbonate, and ether derivatives can be prepared by subsequent reactions of the perhydroxylated B_{12}^{2-} cluster.

A method for the complete cyanation of **1** would be valuable because the resulting dodecacyanododecaborate dianion (**2**,

i.e., $[\text{B}_{12}(\text{CN})_{12}]^{2-}$) is expected to exhibit favorable electronic properties for use as a weak base and WCA, and an electrolyte for lithium- and magnesium-ion batteries. For example, weak basicity of **2** is suggested by computational modeling, which predicts polycyanated boron clusters to be much weaker bases than their boron hydride counterparts.²² In addition, a high stability of **2** to oxidation, a requirement for electrolytes in high-voltage batteries, was predicted by computational studies⁶ and has been further indicated by its experimentally determined electron binding energy of 5.5 eV, the highest value observed for any multiply charged anion.²³

In 1965, Trofimenko's attempts to percyanate the B_{12}^{2-} cluster via UV irradiation of perhalogenated precursors in the presence of KCN resulted in the formation of a mixture of partially cyanated derivatives ($n_{\text{CN}} = 7\text{--}9$).²⁴ A more recent attempt to prepare **2**, also by UV irradiation, led to the observation by mass spectrometry (MS) of **2** as a minor component in a mixture of five different B_{12}^{2-} clusters with the general formula $[\text{B}_{12}(\text{CN})_n(\text{OH})_{12-n}]^{2-}$, where $n = 8\text{--}12$.¹¹ However, the abundance of **2** in the product mixture was low (ca. 10–15% by MS), and it was not isolated. An alternate approach to cyanation, by transition-metal cross-coupling reactions, has been demonstrated with *closo*- CB_{11}^- clusters^{25,26} and *closo*- C_2B_{10} clusters²⁷ but never with the isoelectronic B_{12}^{2-} cluster. We report here a microwave-promoted cross-coupling method for the preparation of **2** and the isolation, spectroscopic characterization, and X-ray crystal structure of this cluster.

The periodinated precursor for cross-coupling reactions, $[\text{B}_{12}\text{I}_{12}]^{2-}$ (**3**), was prepared from commercially available Cs_2I according to published methods.¹⁸ Reacting $[\text{Et}_4\text{N}]_2\text{3}$ with CuCN and $\text{Pd}(\text{Cl})_2$ in *N,N*-dimethylformamide (DMF) under microwave irradiation (MWI) gave **2**, which was isolable as a tetraethylammonium salt in yields of up to 39% (Figure 1).

Investigations of the reaction showed that cyanation depends on several factors. Cyanation reactions of the related CB_{11}^- cluster were previously shown to be sensitive to the cyanide source, proceeding only with CuCN, and failing with NaCN and KCN.²⁵ CuCN was found to be an effective cyanide source for cross-coupling reactions with **3**. Reactions with two additional cyanide sources were not successful: **3** was found to be unreactive with $\text{Zn}(\text{CN})_2$, and it reacted slowly with Et_4NCN , giving only mono- through tricyanated products after heating at 280 °C for 90 min. In contrast to cyanations of the *closo*- CB_{11}^- cluster,²⁵ which proceeded with CuCN in the

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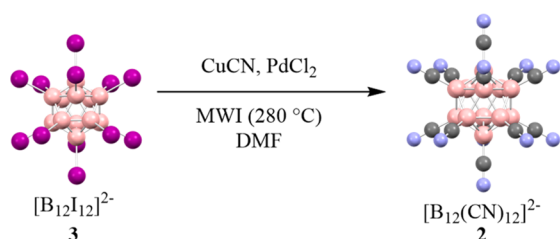


Figure 1. Conditions for the preparation of the percyanoated dianion **2**.

absence of palladium, cyanation of the B_{12}^{2-} cluster required the presence of a palladium catalyst. When carried out on a small scale (20 mg of $[\text{Et}_4\text{N}]_2\mathbf{3}$), substitution of iodine with CN was observed for every palladium catalyst tested. Analysis of the product mixtures by electrospray ionization MS (ESI-MS) indicated a significant degree of polycyanation in all cases: for all catalysts except $\text{PdCl}_2(\text{PhCN})_2$, the fully cyanated cluster **2** was the predominant product in a mixture of clusters with the formula $[\text{B}_{12}(\text{CN})_n\text{I}_{12-n}]^{2-}$ (Figure 2). On a larger

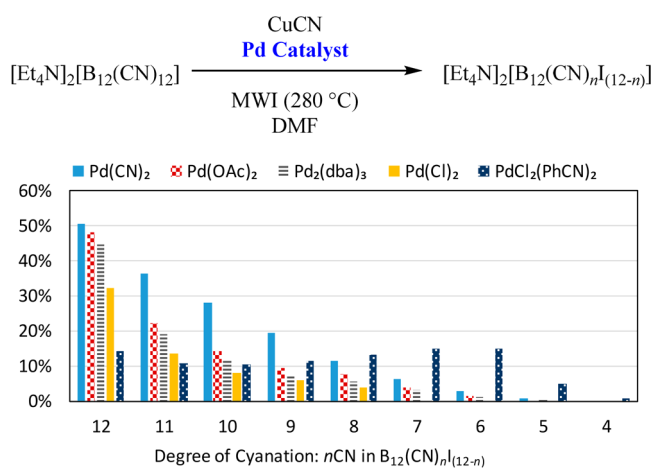


Figure 2. Evaluation of catalysts for cyanation. Reactions were performed with 20 mg of $[\text{Et}_4\text{N}]_2\mathbf{3}$, 15 equiv CuCN, and 25 mol % palladium catalyst in DMF and checked by ESI-MS after 90 min of MWI heating at 280 °C.

scale (0.2 g of $[\text{Et}_4\text{N}]_2\mathbf{3}$), PdCl_2 and $\text{Pd}_2(\text{dba})_3$ gave the most rapid and complete conversion to the fully cyanated $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ product. Even when using the most efficient catalysts, forceful conditions were required, with the reaction only proceeding via MWI at temperatures exceeding 250 °C. Negligible cyanation was observed for all reactions performed under reflux or under lower-temperature MWI ($T < 250$ °C). Dependence of the reaction on the solvent was investigated briefly with three high-boiling-point solvents: DMF, dimethylacetamide, and *N*-methyl-2-pyrrolidone. The formation of **2** as the predominant species in the product mixture was observed for all solvents, and DMF was found to give the most rapid cyanation.

Even under vigorous conditions, driving the reaction to completion proved difficult. Rather than attempt a difficult chromatographic separation of the product mixture, methods for forcing the reaction to proceed further toward a fully cyanated product were explored. Increasing the quantity of CuCN or palladium catalyst loading was not effective, and extending the heating time beyond 90 min also did not result

in further cyanation. Reactions that were monitored at frequent intervals by checking aliquots by liquid chromatography (LC)–MS revealed that the average number of cyano groups achieved a maximum quickly (i.e., after 30 min). Subsequent rounds of heating, with or without the addition of fresh catalyst or more CuCN, did not advance the reaction; in many cases, further heating caused a partial reversion of the reaction, shifting the reaction mixture toward a lower CN:I substitution ratio. The exact cause of this reversion is uncertain, but the significant quantity of iodine liberated during the cyanation reaction was hypothesized to interfere with completion of the reaction. A modified protocol, which included an initial 30 min heating cycle, followed by a wash with aqueous sodium sulfite to remove accumulated iodine, and reheating for 30 min with fresh palladium catalyst and CuCN, was found to reliably convert the starting material to **2**.

The reaction was worked up via a straightforward chromatography-free procedure to give $[\text{Et}_4\text{N}]_2\mathbf{2}$ in reliable yields of 31–39%. The isolated product eluted as a single band in the LC–MS chromatogram with m/z 220.9 ($z = 2$) in the negative-ion MS spectrum, consistent with $[\text{B}_{12}(\text{CN})_{12}]^{2-}$. Characterization by ^{11}B NMR showed a resonance at -17.6 ppm for the product and the disappearance of the resonance at -15.7 ppm for the $[\text{B}_{12}\text{I}_{12}]^{2-}$ starting material. The ^{13}C NMR spectrum contained a resonance at 117 ppm for the carbon in the CN groups; significant broadening of this peak is consistent with one-bond coupling of the C_{CN} nucleus to the attached quadrupolar ^{11}B nucleus. The Fourier transform infrared spectrum of $[\text{Et}_4\text{N}]_2\mathbf{2}$ showed a band at 2235 cm^{-1} , consistent with a $\text{C}\equiv\text{N}$ stretch and in agreement with scaled frequencies of $2255\text{--}2257\text{ cm}^{-1}$ for the $\text{C}\equiv\text{N}$ stretching modes calculated at the B3LYP/6-311+G(d,p) level. Negative-ion high-resolution MS showed an isotopic envelope with a maximum at m/z 221.0784, which is in excellent agreement with the theoretical mass for the most isotopically abundant $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ species (calcd: m/z 221.0777). No other boron clusters were detected by MS.

An alternate workup, which did not include an extraction to remove copper, gave a white solid that was recrystallized from an acetonitrile/water solution to give crystals of $(\text{CH}_3\text{CN})_3\text{Cu}[\mu\text{-B}_{12}(\text{CN})_{12}]\text{Cu}(\text{NCCCH}_3)_3$ suitable for X-ray diffraction (Figure 3). The asymmetric unit of the crystal structure contains one copper atom coordinated to the nitrogen atom in each of three acetonitrile molecules and a nitrogen from one cyano group in **2** in a distorted tetrahedral geometry: $\text{N}\text{--}\text{Cu}\text{--}\text{N}$ angles average 109.43° and range from a min = 102.51° for $\text{N}^9_{\text{CH}_3\text{CN}}\text{--}\text{Cu}\text{--}\text{N}^1_{\text{B}_{12}(\text{CN})}$ to max = 114.21° for $\text{N}^9\text{--}\text{Cu}\text{--}\text{N}^2$. The $\text{Cu}\text{--}\text{N}$ lengths are nearly identical with a longest distance of $1.999(2)$ Å for $\text{Cu}\text{--}\text{N}^1$ and a shortest distance of $1.977(3)$ Å for $\text{Cu}\text{--}\text{N}^2$ and fall within the range of $\text{Cu}\text{--}\text{N}$ distances ($1.964\text{--}2.030$ Å) observed in crystal structures of tetrakis(acetonitrile)copper(I).^{28–32} All $\text{C}\equiv\text{N}$ groups in **2** are essentially linear ($\angle\text{B}\text{--}\text{C}\equiv\text{N} = 177.21\text{--}178.66^\circ$), except for the nitrile group coordinated to the copper center, which is slightly bent ($\angle\text{B}\text{--}\text{C}\equiv\text{N} = 173.84^\circ$). The B_{12}^{2-} core of the cluster is essentially icosahedral in the crystal structure with $\text{B}\text{--}\text{B}$ bond lengths of 1.789 ± 0.012 Å, similar to $\text{B}\text{--}\text{B}$ bond distances for other dodecaborate clusters.^{33,34}

Investigations of **2** demonstrate its stability under a variety of conditions. The ^{11}B NMR spectrum of isolated $[\text{Et}_4\text{N}]_2\mathbf{2}$ was unaffected by treatment with 3 M KOH in 5% aqueous CH_3CN and remained unchanged for over 24 h at room

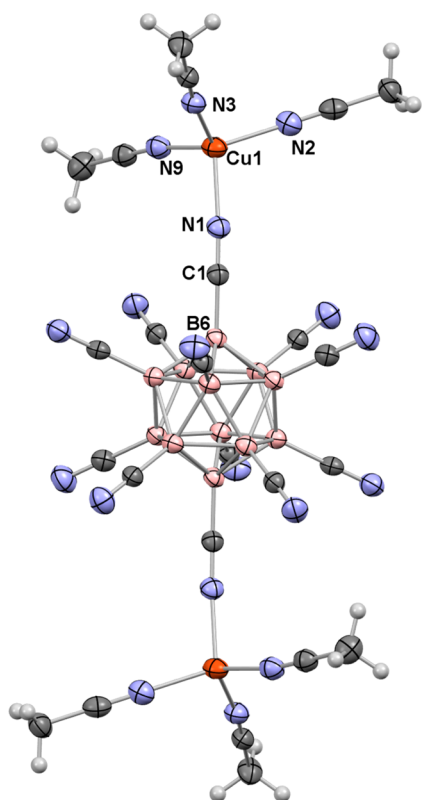


Figure 3. Single-crystal structure of $(\text{CH}_3\text{CN})_3\text{Cu}[\mu\text{-B}_{12}(\text{CN})_{12}]\text{Cu}(\text{CH}_3\text{CN})_3$. Thermal ellipsoids are drawn at the 50% probability level. The asymmetric unit contains a single distorted tetrahedral copper(I) center coordinated to three acetonitrile molecules and one nitrile group from **2**. Two asymmetric units, related by a center of inversion at the center of the B_{12} cluster, comprise the full complex.

temperature. By contrast, the periodinated precursor **3** completely decomposed to $\text{B}(\text{OH})_4^-$ under the same conditions. **2** was also stable in strong aqueous acid, showing no change for over 24 h at room temperature in 50% H_2SO_4 . Likewise, **2** did not react for over 24 h when treated with excess aqueous Ce^{4+} or with sodium metal in tetrahydrofuran.

The stability of **2** in acid suggested the possibility of converting its CN groups to carboxylic acids by acid-catalyzed hydrolysis, an approach that has previously been used to prepare carboxylated CB_{11}^- clusters.^{25,35,36} Hydrolyses of **2** in an hydrochloric acid/acetic acid solution were attempted under both MWI and conventional heating. LC–MS monitoring of MWI reactions showed product mixtures containing unreacted **2** as well as clusters with one or two COOH groups (in abundances of up to ca. 40% and 20%, respectively). However, significant decomposition of **2** to $\text{B}(\text{OH})_3$ occurred after only 30 min of MWI heating at 180 °C. Negligible decomposition was observed for conventionally heated reactions, but these required reflux for 2 weeks to achieve a comparable product mixture.

In summary, we have demonstrated that the peryanated dianion **2** can be prepared by microwave-promoted palladium-catalyzed cross-coupling reactions. The isolation of this cluster in a pure form represents an important step toward its use in applications, including as a WCA and in lithium- and magnesium-ion batteries. We are currently investigating polycyanation of other boron clusters, which should be possible using this procedure.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03037>.

Experimental details, NMR, IR, and mass spectra, and X-ray crystallographic data (PDF)

Accession Codes

CCDC 1956907 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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