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N-arylammonio- and *N*-pyridinium-substituted derivatives of dodecahydro-*closo*-dodecaborate(2-)

Andrea Vöge [a,*], Enno Lork [a], Behice Şebnem Sesalan [b], Detlef Gabel [a]

[a] Department of Chemistry, University of Bremen, Leobener Str. NW2 C3020, D-28357 Bremen, Germany
[b] Department of Chemistry, Technical University of Istanbul, Maslak 34469, Istanbul, Turkey

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ABSTRACT

We report two methods for preparing *N*-arylammonio, *N*-pyridyl and *N*-arylamino dodecaborates: heating of the tetrabutylammonium salt of dodecahydro-*closo*-dodecaborate(2-) with aryl and pyridyl amines, or nucleophilic attack of [*closo*-$B_{12}H_{11}NH_2]^{2-}$ on a strongly deactivated aromatic system. With aryl amines we obtained [1-*closo*-$B_{12}H_{11}N(R^1)_2C_6H_5]^-$ (R^1 = H, CH_3). With 4-(dimethylamino)pyridine, [1-*closo*-$(B_{12}H_{11}NC_5H_4)$-4-$N(CH_3)_2]^-$, with a bond between the boron and the pyridinium nitrogen, was obtained. A presumable mechanism for this kind of reactions is reported. By nucleophilic substitution, two products, [1-*closo*-$(B_{12}H_{11}NHC_6H_3)$-3,4-$(CN)_2]^{2-}$ and [1-*closo*-$(B_{12}H_{11}NHC_6H_2)$-2-(NO_2)-4,5-$(CN)_2]^{2-}$, were formed with 4-nitrophthalonitrile and 1-chloro-2,4-dinitrobenzene gave [1-*closo*-$(B_{12}H_{11}NHC_6H_3)$-2,4-$(NO_2)_2]^{2-}$. For [1-*closo*-$B_{12}H_{11}N(CH_3)_2C_6H_5]^-$ and [1-*closo*-$(B_{12}H_{11}NHC_6H_3)$-2,4-$(NO_2)_2]^{2-}$ single crystal X-ray structures were obtained.

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1. Introduction

The icosahedral dodecahydro-*closo*-dodecaborate(2-) possesses unique properties, such as chemical, hydrolytical and thermal stability and low toxicity. These properties make the cluster and its derivatives useful for various applications, such as boron neutron capture therapy (BNCT), e.g., the [*closo*-$B_{12}H_{11}SH]^{2-}$ is the most widely used agent in this kind of cancer therapy [1]. There are several routes for a substitution at the cluster: formation of boron–oxygen [2–4], –sulfur [5], –halogen [6], –phosphorus [7], –carbon [8,9], and –nitrogen [10–12] bonds.

Relatively little work has been directed towards the optical properties of the [*closo*-$B_{12}H_{12}]^{2-}$ derivatives. Calculations predict large hyperpolarizability (β) values [13] and Bernard et al. demonstrated the donor potential of the B_{12} cluster by linear absorption studies of cluster containing non-centrosymmetric π-conjugated systems [14], so the cluster in combination with acceptor substituents promises to be an interesting new electron donor for non-linear optical materials.

N,N,N-trialkylammonioundecahydro-*closo*-dodecaborates(1-) [15] represent a new type of anions for use as ionic liquids [16,17]. The alkylated cluster derivatives can easily be obtained by refluxing the sodium salt of [*closo*-$B_{12}H_{12}]^{2-}$ with hydroxylamine-*O*-sulfonic acid [10] followed by alkylation of [*closo*-$B_{12}H_{11}NH_3]^-$ with alkyl halide in the presence of a base. Dependent on the base and the branching of the alkyl chain *N*-alkylation will occur two or three times. A pure monoalkylated product can only be achieved by the reaction of [*closo*-$B_{12}H_{12}]^{2-}$ with metylhydroxylamine-*O*-sulfonic acid [16] to the monomethylated product or, limited to aromatic aldehydes, by reduction of the Schiff base to give the monobenzyl derivatives [18]. In this paper we report that a nucleophilic attack of [*closo*-$B_{12}H_{11}NH_2]^{2-}$ on a benzene derivative with electron withdrawing substituents results in *N*-aryl cluster derivatives.

In a second kind of reaction a boron–nitrogen bond was formed by heating the tetrabutylammonium salt of the cluster with aryl and pyridyl amines, leading to *N*-monophenyl and pyridyl derivatives of the cluster. Prior to our work, a direct boron–nitrogen–aryl connection was described by Drozdova et al., who prepared [1-*closo*-$(B_{12}H_{11}N(MePh(CH_2Cl))]^-$ via a Vilsmeyer reaction [19] and Preetz and Koch [11,12].

Preetz and Koch have found a direct *N*-attachment of 2,2′-bipyridine with the dodecaborate cluster [11]. The reaction with 4-aminopyridine led to [1-*closo*-$B_{12}H_{11}NHC_5H_4N]^-$ [12]. In contrast, we found that the reaction of dodecaborate with 4-(dimethylamino)pyridine does not lead to a boron–nitrogen bond to the amino group, but to the nitrogen atom of the pyridine. A presumable mechanism which is described in the discussion part of this article might explain these unexpected differences.

The method which we have developed offers a wide variety of possibilities for the preparation of new cluster derivatives, which are promising boron moieties for a number of applications, e.g., as ionic liquids, in non-linear optics and also for BNCT. The pht-

* Corresponding author. Tel.: +49 421 218 2381.
E-mail address: andreavoege@online.de (A. Vöge).

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halonitrile derivatives of the cluster could be precursors of phthalocyanines and porphyrazines. Porphyrazines and phthalocyanines carrying boron clusters were prepared by Semioshkin et al. [20], and Bregadze et al. [21].

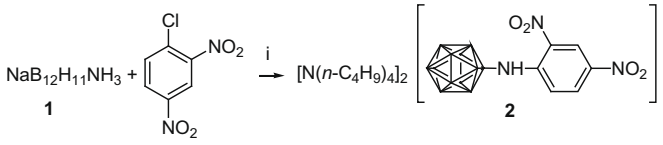
2. Results and discussion

2.1. Nucleophilic aromatic substitutions

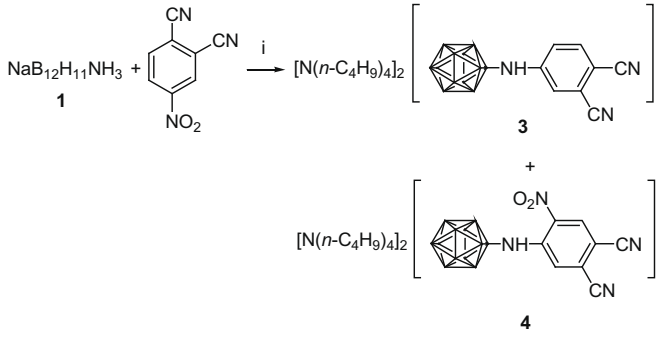
[*closo*-$B_{12}H_{11}NH_3$]$^-$ **1**, first described by Hertler and Raasch [10], is known as a strong nucleophile [15,16,22]. For maximal nucleophilicity a strong base such as KOH, NaOEt or NaH is required.

One method for the synthesis of monoarylated **1** is the nucleophilic aromatic substitution of [*closo*-$B_{12}H_{11}NH_2$]$^{2-}$ with 1-chloro-2,4-dinitrobenzene (Scheme 1) and leads to **2**. The similar reaction of **1** with 4-nitrophthalonitrile (Scheme 2) results in a mixture of two compounds, which can be separated by column chromatography: one is the result of a nucleophilic substitution of the nitro group **(3)** and the other of a nucleophilic attack of the nitrogen of deprotonated **1** on the carbon with the highest partial positive charge and least steric hindrance at the aromatic system, leading to **4**.

The reaction proceeds as a nucleophilic aromatic substitution. The presence of electron withdrawing substituents, in this case cyano or nitro groups, located at the benzene is necessary to allow for the nucleophilic attack. In the case of **4** the amino group attacks the carbon at the *ortho* position to the nitro group and a hydride leaves the aromatic system, forming molecular hydrogen with the proton of the amino group. The evidence for the attack at this carbon is seen in the ^{1}H NMR spectrum: there are two singlets for the protons of the aromatic system with no coupling between them. Because of the donor–acceptor properties of these three compounds (the dodecaborate cluster acts as a donor [14] and cyano and nitro groups as acceptors which are connected via a π-conjugated system), they might be useful for non-linear optical materials. Usually **1** and its derivatives, e. g., Schiff bases or mono- and dialkylated **1**, are *N*-protonated because of the high pK_a value of the amino group. ^{1}H NMR and ESI spectra analyses show that in **2**, **3** and **4**, the nitrogen is not protonated. In these amino derivatives formed, electronic interaction between the cluster and the aromatic ring is probable, because of their intense color (compound **2** and **4** are dark red and **3** is brown), in contrast to the *N*-protonated compounds **6** and **7** described below, which are colorless. We attribute this to the presence of the strongly electron-withdrawing groups in **2**, **3**, and **4**. The molar extinction coefficient of **2** is 16129 L mol^{-1} cm^{-1} in methanol with an absorption maximum at 395 nm.



Scheme 1. Nucleophilic aromatic substitution. i 1. NaOEt/EtOH; 2. DMSO; 3. [N(*n*-C_4H_9)$_4$]Br/H_2O.



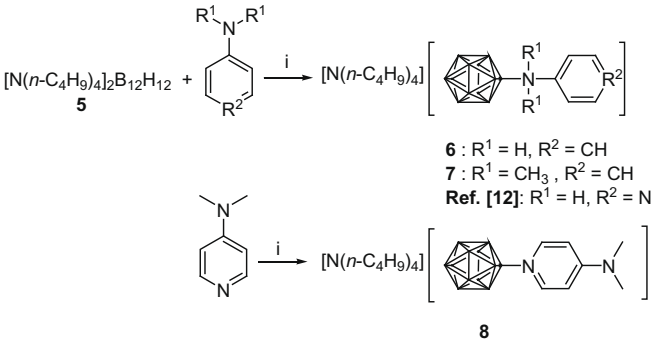
Scheme 2. Nucleophilic aromatic substitution. i 1. NaOEt/EtOH; 2. DMSO; 3. [N(*n*-C_4H_9)$_4$]Br/H_2O.

2.2. Reaction of [N(*n*-C_4H_9)$_4$]$_2$$B_{12}H_{12}$ (**5**) with aryl amines and pyridine amines

Aryl amines (aniline and *N,N*-dimethylaniline) react at high temperatures (in the absence of additional solvent) with the tetrabutylammonium salt of dodecahydro-*closo*-dodecaborate(2-), **5**, to *N*-phenylammonio derivatives (Scheme 3). Dependent on the duration of heating, amination does not stop at the mono-substituted derivatives.

With 4-(dimethylamino)pyridine, substitution does not take place at the amino nitrogen, but rather at the pyridine nitrogen, resulting in **8**, a pyridinium-substituted boron cluster (Scheme 3). The ^{13}C NMR spectra confirm that in this case the pyridine nitrogen attacks the boron atom at the cluster: the chemical shift of the methyl groups of the quaternary ammonio group of **7** is definitely shifted to high field (δ = 56.01 ppm) compared to the methyl groups of **8** (δ = 38.97 ppm), which is a tertiary amine. Koch and Preetz described the reaction of the cluster with 4-aminopyridine [12] and found that the attachment occurred *via* the amino nitrogen, in contrast to our results with 4-(dimethylamino)pyridine. We assume that this difference is caused by different mechanisms of the reactions.

The introduction of heteroatoms on the dodecaborate cluster usually occurs through a nucleophilic attack of the cluster on compounds with a partially positively charged heteroatom, such as the nitrogen in the synthesis of the unsubstituted ammonio cluster, in which hydroxylamine-*O*-sulfonic acid is used [10]. In the cases described here, the mechanism must be different, because there are no positive partial charges on the nitrogen atoms; rather, the aryl amines and the pyridine react as nucleophiles. The reaction with 4-(dimethylamino)pyridine and *N,N*-dimethylaniline is only successful with the tetrabutylammonium salt of the cluster; with other cations such as sodium and tetramethylammonium, no reaction takes place. We speculate that, at high temperatures of the reactions (around 200 °C), a hydride ion might be released from the cluster, acting as base and leading to a Hofmann elimination of butene from the tetrabutylammonium cation. The positively charged boron atom left behind might then react as electrophile and can be attacked by the *N*-atom of the amino group and pyri-



Scheme 3. Reaction of [*closo*-$B_{12}H_{12}$]$^{2-}$ with aniline, *N,N*-dimethylaniline, 4-aminopyridine [12] and 4-(dimethylamino)pyridine. i 200 °C or reflux.

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