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

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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.

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-

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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].

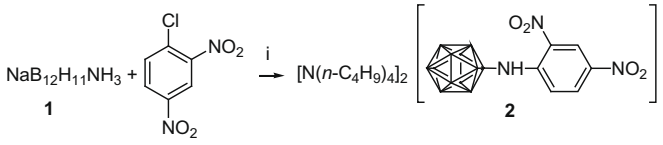
2. Results and discussion

2.1. Nucleophilic aromatic substitutions

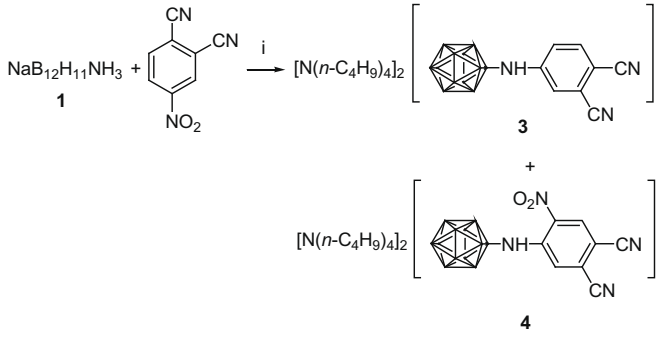
[*closo*-$B_{12}H_{11}NH_3$]$^-$ **1**, first described by Hertler and Raasch [10], is known as a strong nucleophile [15,16,22]. For maximal nucleophilicity a strong base such as KOH, NaOEt or NaH is required.

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.



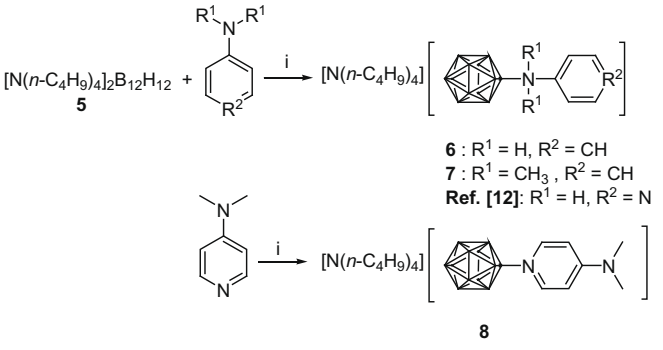
Scheme 2. Nucleophilic aromatic substitution. i 1. NaOEt/EtOH; 2. DMSO; 3. [N(*n*-C_4H_9)$_4$]Br/H_2O.

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-



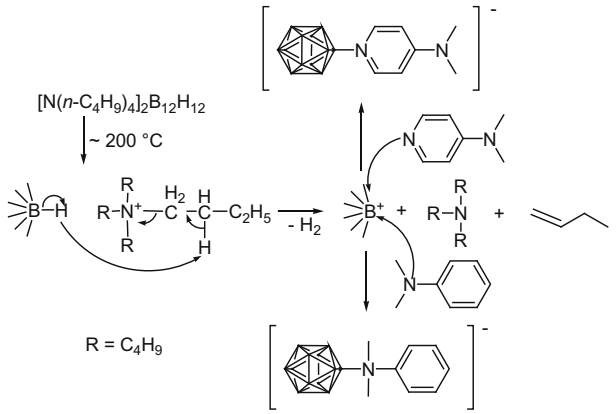
Scheme 3. Reaction of [*closo*-$B_{12}H_{12}$]$^{2-}$ with aniline, *N,N*-dimethylaniline, 4-aminopyridine [12] and 4-(dimethylamino)pyridine. i 200 °C or reflux.

dine, respectively (Scheme 4). In the case of 4-(dimethylamino)pyridine, the reaction occurs at the pyridine nitrogen as it is more nucleophilic than that of the amino group.

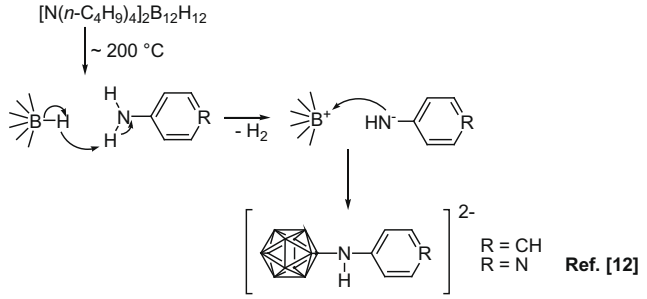
The product described by Koch and Preetz [12] seems, at a first glance, surprising because the pyridine nitrogen has a higher nucleophilicity and should therefore react first with the electrophilic boron atom. We think that this can be explained by a difference in mechanism of the two reactions: when there are hydrogen atoms at the amino groups (aniline, 4-aminopyridine) the forming hydride of the cluster attacks these first to form dihydrogen; an abstraction of a proton of the tetrabutylammonium (first step of the Hofmann elimination), observed in the case of 4-(dimethylamino)pyridine and *N,N*-dimethylaniline, would then no longer occur. After deprotonation, the amino nitrogen is now more nucleophilic than the pyridine nitrogen, and will react with the positively charged boron atom (Scheme 5). The same mechanism applies for the reaction with aniline (in which the strongest nucleophile is the single nitrogen atom).

With aniline derivatives, two types of further products were observed in ESI mass spectra: derivatives with additional butyl groups. These side products are obtained subsequent to the reaction of the cluster with aniline (Scheme 3), where further heating leads to Hoffmann elimination of the tetrabutylammonium cation, as found in the reaction with 4-(dimethylamino)pyridine and *N,N*-dimethylaniline. Derivatives where the cluster is multiply substituted were found as well. Further evidence for Hofmann elimination is the appearance of a peak with *m*/*z* 186 in positive ESI mass spectra which corresponds to the resulting tributylammonium cation (Scheme 6).

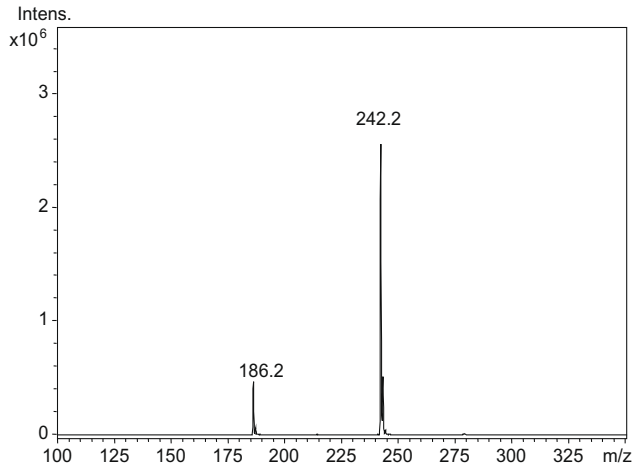
In negative ESI mass spectrum (Scheme 7), signals of compounds with additional butyl groups are found, which can be



Scheme 4. Mechanism for the reaction of $[N(n\text{-}C_4H_9)_4]_2B_{12}H_{12}$ with 4-(dimethylamino)pyridine and *N,N*-dimethylaniline via Hofmann elimination of butene.



Scheme 5. Mechanism for the reaction of $[N(n\text{-}C_4H_9)_4]_2B_{12}H_{12}$ with 4-aminopyridine [12] and aniline.

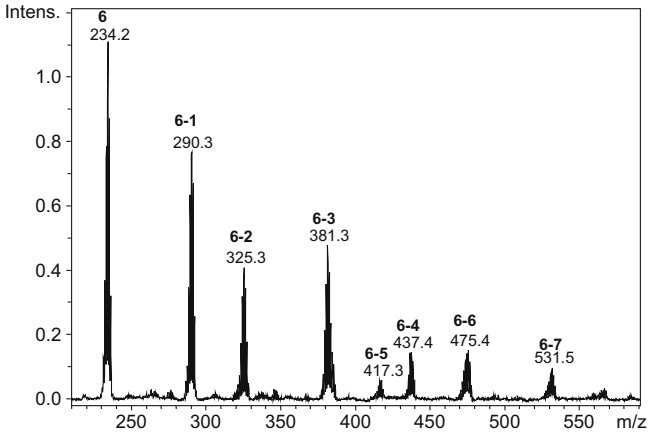


Scheme 6. $(n\text{-}C_4H_9)_3NH^+$ (m/z = 186, tributylammonium) and $(n\text{-}C_4H_9)_4N^+$ (m/z = 242, tetrabutylammonium) in ESI mass spectrum (positive mode).

attributed to hydroamination of butene. Three hours of heating the cluster with aniline leads only to reactant, $[B_{12}H_{12}]^{2-}$, and the product **6**. When heating is prolonged overnight, **6** and several additional side products are detected in the ESI mass spectrum (Scheme 7). The peak of the anion of **6** (m/z 234) appears together with its mono-hydroamination product **6-1** $[B_{12}H_{11}NHBuC_6H_5]^-$ with m/z 290, a disubstitution product **6-2** $[B_{12}H_{10}(NHC_6H_5)(NH_2C_6H_5)]^-$ with m/z 325, and its mono- and dihydroamination products **6-3** $[B_{12}H_{10}(NHC_6H_5)(NHBuC_6H_5)]^-$ with (m/z 381), and **6-4** $[B_{12}H_{10}(NHBuC_6H_5)(NBuC_6H_5)]^-$ with m/z 437. Also the trisubstitution product **6-5** $[B_{12}H_9(NHC_6H_5)_2(NH_2C_6H_5)]^-$ with m/z 417, and its mono- and dihydroamination products **6-6** $[B_{12}H_9(NHC_6H_5)_2(NHBuC_6H_5)]^-$ with m/z 475 and **6-7** $[B_{12}H_9(NHBuC_6H_5)_2(NHC_6H_5)]^-$ with m/z 531 are found.

When the cluster reacts with electrophiles, e.g., the amino group of the hydroxylamine-*O*-sulfonic acid, a second substitution takes place at the boron atom 7, and a third reaction at B-9 [10]. In the multiply substituted products reported here, we do not know the substitution pattern, as the cluster reacts with a nucleophile. In the case of **6-3**, **6-6** und **6-7**, protonation could occur at different N atoms. We suggest that protonation occurs on a tertiary amine, as this should be more nucleophilic.

The positive ESI mass spectra of tetrabutylammonium derivatives of the dodecaborate cluster are usually dominated by the



Scheme 7. ESI mass spectrum (negative mode) for overnight reaction of $[N(n\text{-}C_4H_9)_4]_2B_{12}H_{12}$ with aniline.

Table 1
Crystallographic data for $[N(n\text{-}C_4H_9)_4]_2[1\text{-}closo\text{-}(B_{12}H_{11}NHC_6H_3)\text{-}2,4\text{-}(NO_2)_2]$ (**2**) and $N(n\text{-}C_4H_9)_4$ $[1\text{-}closo\text{-}B_{12}H_{11}N(CH_3)_2C_6H_5]$ (**7**).

	2	**7**
Formula	$C_{38}H_{87}B_{12}N_5O_4$	$C_{24}H_{58}B_{12}N_2$
Formula weight	807.85	504.44
T (K)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (pm)	2071.6(3)	1085.7(3)
b (pm)	1384.4(5)	2038.6(3)
c (pm)	1848.7(3)	1482.0(4)
V (nm^3)	5.09(1)	3.2458(13)
Z	4	4
D_{calc} (Mg/m^3)	1.055	1.032
Absorption coefficient (mm^{-1})	0.063	0.053
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
R [$I > 2\sigma(I)$]	0.1348	0.0685
R_w (all data)	0.4168	0.2009

peak m/z 242 of the tetrabutylammonium cation. After the reaction with 4-(dimethylamino)pyridine its peak has disappeared, and a single other peak, with m/z 179 which belongs to $(H_3C)_2NC_5H_4N^+(n\text{-}C_4H_9)$, occurs. As the corresponding peaks are not found in the reactions with aniline, and *N,N*-dimethylaniline, respectively, we assume that the butene which appears during the Hofmann elimination reacts with the pyridine nitrogen rather than with the nitrogen of the amino groups.

2.3. X-ray structure analyses of $[N(n\text{-}C_4H_9)_4]_2[1\text{-}closo\text{-}(B_{12}H_{11}NHC_6H_3)\text{-}2,4\text{-}(NO_2)_2]$ (**2**) and $N(n\text{-}C_4H_9)_4$ $[1\text{-}closo\text{-}B_{12}H_{11}N(CH_3)_2C_6H_5]$ (**7**)

Crystals of **2** and **7** could be achieved as tetrabutylammonium salts from methanol and single crystal X-ray structure analyses of these compounds were carried out (Table 1). The cluster anions of **2** and **7** are shown in Figs. 1 and 2. Selected bond lengths and angles for **2** and **7** are given in Tables 2 and 3, respectively.

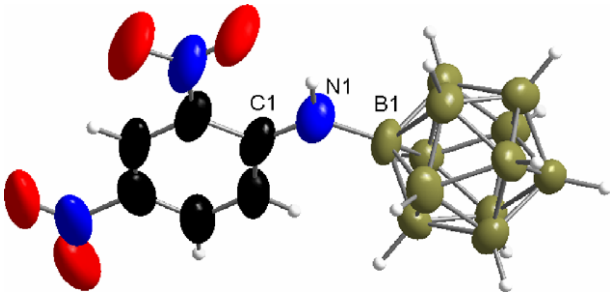


Fig. 1. Molecular structure of $[1\text{-}closo\text{-}(B_{12}H_{11}NHC_6H_3)\text{-}2,4\text{-}(NO_2)_2]^{2-}$ anion (**2**).

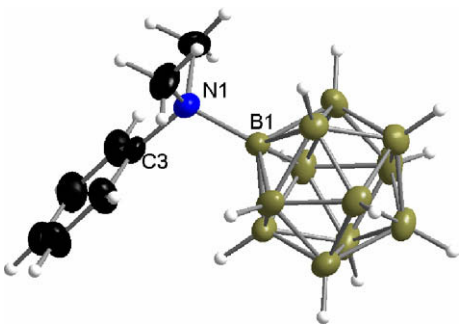


Fig. 2. Molecular structure of $[1\text{-}closo\text{-}B_{12}H_{11}N(CH_3)_2C_6H_5]^-$ anion (**7**).

Table 2
Selected bond lengths (pm) and angles (°) for the $[1\text{-}closo\text{-}(B_{12}H_{11}NHC_6H_3)\text{-}2,4\text{-}(NO_2)_2]^{2-}$ (**2**) anion.

Bond lengths			
B(1)–N(1)	152.5(12)	N(2)–O(1)	123.0(11)
N(1)–C(1)	133.2(11)	N(2)–O(2)	124.6(11)
C(2)–N(2)	143.8(14)	N(3)–O(3)	124.3(14)
C(4)–N(3)	148.1(15)	N(3)–O(4)	121.7(14)
B–B	173.0(15)–181.5(13)		
Bond angles			
C(1)–N(1)–B(1)	131.3(8)	O(1)–N(2)–C(2)	121.4(10)
N(1)–C(1)–C(6)	122.5(8)	O(2)–N(2)–C(2)	118.9(12)
N(1)–C(1)–C(2)	124.5(10)	O(4)–N(3)–C(4)	117.1(15)
C(3)–C(2)–N(2)	117.0(11)	O(3)–N(3)–C(4)	117.5(14)
N(2)–C(2)–C(1)	120.8(11)	N(1)–B(1)–B(2)	128.7(8)
C(3)–C(4)–N(3)	119.3(14)		

In Table 4, a comparison of the structure around the central nitrogen atom is shown.

Although the quality of the crystals of **2** was not optimal, the differences in bond lengths and bond angles are significant. The planes of the aromatic rings are oriented differently in **2** and **7**: in **7**, the ring is oriented in relation to the cluster such that the interactions between the hydrogen atoms (and thus the steric strain) are minimized. In contrast, the *ortho* hydrogen atom of the ring in **2** points toward the cluster. In addition, the bond lengths B–N and N-C in **2** are shorter than in **7** and thus appear to have a higher degree of double bond character. Also, in **2** the B–N–C angle is widened from a tetrahedral value. Thus, in **2** there is a possibility for electronic interaction between the cluster and the dinitrophenyl ring. Such interaction might be responsible for the strongly red-shifted absorption of **2**. In **7**, this angle is nearly that of an ideal tetrahedron.

The structure around the central nitrogen atom of **2** is very similar to that of the Schiff bases published by Sivaev et al. [18] and the

Table 3
Selected bond lengths (pm) and angles (°) for the $[1\text{-}closo\text{-}B_{12}H_{11}N(CH_3)_2C_6H_5]^-$ (**7**) anion.

Bond lengths			
B(1)–N(1)	162.4(3)	C(3)–C(4)	137.3(3)
N(1)–C(1)	151.2(3)	C(3)–C(8)	138.1(3)
N(1)–C(2)	149.3(3)	C(4)–C(5)	138.4(4)
N(1)–C(3)	149.5(3)	C(5)–C(6)	137.5(4)
		C(6)–C(7)	136.6(4)
B–B	176.1(3)–179.2(4)	C(7)–C(8)	139.8(4)
Bond angles			
C(2)–N(1)–C(3)	110.95(18)	C(4)–C(3)–C(8)	119.2(2)
C(2)–N(1)–C(1)	105.2(2)	C(4)–C(3)–N(1)	121.4(2)
C(3)–N(1)–C(1)	109.34(18)	C(8)–C(3)–N(1)	119.4(2)
C(2)–N(1)–B(1)	110.13(17)	C(3)–C(4)–C(5)	120.7(2)
C(3)–N(1)–B(1)	110.94(15)	C(6)–C(5)–C(4)	120.5(2)
C(1)–N(1)–B(1)	110.16(17)	C(7)–C(6)–C(5)	119.0(2)
N(1)–B(1)–B(2)	121.37(17)	C(6)–C(7)–C(8)	121.0(3)
C(3)–C(8)–C(7)	119.6(2)		

Table 4
Comparison of bond lengths (Å) and angles (°) around the central nitrogen atom of the anions of **2**, **7**, Schiff base[a], and aminopyridine derivative[b]

	2	**7**	Schiff base[a]	Aminopyridine derivative[b]
B–N	1.52	1.62	1.52	1.51
N–C	1.33	1.49	1.27	1.38
B–N–C	130	111	129	133

[a] Compound $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]^-$ [18].
[b] Compound $(Ph_4As)[(4\text{-}(NH)\text{-}C_5H_4N)B_{12}H_{11}] \cdot 2CH_3CN$ [12].

4-aminopyridine cluster derivative described by Preetz and Koch [12].

3. Experimental

3.1. General

$Cs_2B_{12}H_{12} \cdot CH_3OH$ was purchased from BASF (Ludwigshafen, Germany). Cation exchange was performed by dissolving the cesium salt in hot water followed by addition of a concentrated aqueous solution of tetrabutylammonium bromide in a molar ratio of 1:2 to obtain compound **5**.

The tetrabutylammonium salt of [*closo*-$B_{12}H_{11}NH_3$]$^-$ was prepared by addition of an aqueous solution of tetrabutylammonium bromide to a hot aqueous solution of Cs[*closo*-$B_{12}H_{11}NH_3$] obtained as described in the literature [10]. The sodium salt **1** was obtained by ion exchange with sodium tetraphenylborate in water and dichloromethane as two-phase system.

The purity of compounds was assessed by ESI mass spectrometry, ^{1}H, ^{13}C, ^{11}B NMR and IR spectroscopy and X-ray analysis as it is known that the elemental analysis of dodecaborate-containing compounds is not reliable [23]. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 200 spectrometer at 200, 50, and 64 MHz and on a Bruker Avance WB-360. Infrared spectra of KBr pellet were collected on a Bio Rad FTS-IR 155 spectrometer. ESI mass spectra were obtained on a Bruker Esquire spectrometer. The *m*/*z* listed below are those of the most intense peak of the isotope pattern. X-ray analyses were carried out with a Siemens P4 four circle diffractometer. Silica gel Normasil 40–63 μm, Prolabo Chemicals, was used for column chromatography.

3.2. $[N(n\text{-}C_4H_9)_4]_2$[1-*closo*-($B_{12}H_{11}NHC_6H_3$)-2,4-(NO_2)$_2$] (**2**)

0.50 g (0.0028 mol) of **1** was stirred with 0.19 g (0.0028 mol) sodium ethanolate in ethanol overnight. The solvent was removed and the residue was dried in vacuum. The resulting solid and 0.62 g (0.0030 mol) 1-chloro-2,4-dinitrobenzene were dissolved in 8 ml dry DMSO each and combined. The red brown mixture was stirred overnight and the solvent was removed, followed by dissolving the residue in water and extraction with dichloromethane. Tetrabutylammonium bromide (0.90 g, 0.0028 mol) was dissolved in a minimal amount of water and added to the water fraction to precipitate the red colored product **2**.

Yield: 0.83 g (1.03 mmol, 37%). ^{1}H NMR (CD_3CN, ppm): 8.96 (br, 1H, N*H*), 8.86 (d, 1H, $C_{Ar}NO_2C_{Ar}HC_{Ar}NO_2$), 8.29 (d, 1H, $C_{Ar}HC_{Ar}HC_{Ar}NO_2$), 7.91 (d/d, 1H, $NHC_{Ar}H$), 3.08 (m, 16H, NCH_2), 1.60 (m, 16H, NCH_2CH_2), 1.34 (st, 16H, $NCH_2CH_2CH_2$), 0.96 (t, 24H, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, ppm): 153.73 ($C_{Ar}NH$), 130.03 ($HNC_{Ar}C_{Ar}NO_2$), 129.13 ($HC_{Ar}C_{Ar}NO_2$), 128.71 ($HC_{Ar}C_{Ar}HC_{Ar}NO_2$), 125.74 ($HNC_{Ar}C_{Ar}H$), 121.86 ($O_2NC_{Ar}C_{Ar}HC_{Ar}NO_2$), 59.70 ($NCH_2$), 24.69 ($NCH_2CH_2$), 20.71 ($NCH_2CH_2CH_2$), 14.19 ($CH_3$). ^{11}B{^{1}H} NMR ($CD_3CN$, ppm): −4.89 (1 B, *B*N), −15.21, −15.61, −17.30 (11 B, *B*H). IR (KBr, cm^{-1}): 3338 (m, ν (NH)), 2963, 2935, 2875 (m, ν (CH_2, CH_3)), 2482 (s, ν (BH)), 1617 (m, ν (C═C_{Ar})), 1575, 1526 (m, ν (N═O)), 1320 (s, ν (N═O)). MS (ESI) negative, *m*/*z*: 141 ($B_{12}H_{11}^-$), 161 (A^{2-}), 182 ($HNC_6H_3(NO_2)_2^-$), 252 (A^{2-} + $HNC_6H_3(NO_2)_2^-$), 565 (A^{2-} + $N(n\text{-}C_4H_9)_4^+$), positive: 242 ($N(n\text{-}C_4H_9)_4^+$). M.p.: 97 °C.

3.3. $[N(n\text{-}C_4H_9)_4]_2$[1-*closo*-($B_{12}H_{11}NHC_6H_3$)-3,4-(CN)$_2$] (**3**) and Cs_2[1-*closo*-($B_{12}H_{11}NHC_6H_2$)-2-(NO_2)-4,5-(CN)$_2$] (**4**)

0.50 g (0.0028 mol) of **1** was stirred with 0.19 g (0.0028 mol) sodium ethanolate in ethanol overnight. The solvent was removed and the residue was dried in vacuum. The resulting solid and 0.52 g (0.0030 mol) 4-nitrophthalonitrile were dissolved in 8 ml dry DMSO each and combined. The mixture was stirred overnight and the solvent was removed, followed by dissolving the residue in water and extraction with dichloromethane. 1.81 g (0.0056 mol) tetrabutylammonium bromide was dissolved in a minimal amount of water and added to the water solution to precipitate the red colored mixture of products **3** and **4**, which was purified by column chromatography on silica gel with CH_3CN and CH_2Cl_2 (1:7.8). To remove the reactant 4-nitrophthalonitrile from **4**, the red colored residue was dissolved in methanol and **4** precipitated with a concentrated solution of cesium fluoride in methanol (1:2).

Compound **3** Yield: 0.15 g (0.20 mmol, 7%). ^{1}H NMR (CD_3CN, ppm): 7.23 (m, 3H, CH_{Ar}), 5.01 (br, 1H, N*H*), 3.08 (m, 16H, NCH_2), 1.60 (m, 16H, NCH_2CH_2), 1.35 (st, 16H, $NCH_2CH_2CH_2$), 0.97 (t, 24H, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, ppm): 157.27 (NHC_{Ar}), 136.04 ($C_{Ar}HC_{Ar}CN$), 134.72 ($C_{Ar}CN$), 129.78 ($HNC_{Ar}C_{Ar}H$), 129.56 ($HNC_{Ar}C_{Ar}H$), 120.29 (*C*N), 94.43 ($C_{Ar}CN$), 59.67 (NCH_2), 24.66 (NCH_2CH_2), 20.67 ($NCH_2CH_2CH_2$), 14.16 (CH_3). IR (KBr, cm^{-1}): 3401 (w, ν (NH)), 2964, 2937, 2876 (m, ν (CH_2, CH_3)), 2480 (s, ν (BH)), 2209 (m, ν (CN)), 1593 (m, ν (C═C_{Ar})). MS (ESI) negative, *m*/*z*: 142 (A^{2-}), 526 (A^{2-} + $N(n\text{-}C_4H_9)_4^+$), positive: 242 ($N(n\text{-}C_4H_9)_4^+$). M.p.: 112 °C.

Compound **4** Yield: 0.25 g (0.42 mmol, 15%). ^{1}H NMR (DMSO-d_6, ppm): 8.73 (s, 1H, N*H*), 8.67 (s, 1H, CH_{Ar}), 8.48 (s, 1H, CH_{Ar}), 2.40, −0.32 (br, 11H, B*H*). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm): 149.24 (NHC_{Ar}), 133.91 ($O_2NC_{Ar}C_{Ar}H$), 130.24 ($C_{Ar}NO_2$), 127.53 ($HNC_{Ar}C_{Ar}H$), 116.79 (*C*N), 116.52 ($C_{Ar}CN$), 115.72 (*C*N), 92.61 ($C_{Ar}CN$). ^{11}B{^{1}H} NMR (DMSO-d_6, ppm): −5.10 (1 B, *B*N), −15.54 (11 B, *B*H). IR (KBr, cm^{-1}): 3322 (w, ν (NH)), 2491 (s, ν (BH)), 2225 (m, ν (CN)), 1619 (m, ν (C═C_{Ar})), 1560 (m, ν (N═O)). MS (ESI) negative, *m*/*z*: 141 ($B_{12}H_{11}^-$), 164 (A^{2-}), 187 ($HNC_6H_2(NO_2)(CN)_2^-$), 461 (A^{2-} + Cs^+), positive: 133 (Cs^+). M.p.: >250 °C.

3.4. $[N(n\text{-}C_4H_9)_4]$[*closo*-$B_{12}H_{11}NH_2C_6H_5$] (**6**)

2.00 g (0.0032 mol) of **5** was stirred and refluxed with 5.2 ml (0.0570 mol) aniline (bp. 182 °C) for 3 h, cooled, stirred in diethylether and filtered. The residue was extracted with dichloromethane and diluted hydrochloric acid. For further purification column choromatography on silica gel with CH_3CN and CH_2Cl_2 (1:7.8) was carried out. The second fraction contains the product and the oily residue was stirred in diethylether to give **6** as a colorless solid.

Yield: 0.25 g (0.53 mmol, 16%). ^{1}H NMR (DMSO-d_6, ppm): 8.42 (s, 2H, N*H*), 7.2 (m, 5H, CH_{Ar}), 3.14 (m, 8H, NCH_2), 1.54 (m, 8H, NCH_2CH_2), 1.30 (st, 8H, $NCH_2CH_2CH_2$), 1.06 (t, 12H, CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm): 139.65 (H_2NC_{Ar}), 127.91 ($NHC_{Ar}HC_{Ar}C_{Ar}H$), 125.77 ($NHC_{Ar}HC_{Ar}C_{Ar}H$), 123.63 ($H_2NC_{Ar}C_{Ar}H$), 57.50 (NCH_2), 23.02 (NCH_2CH_2), 19.16 ($NCH_2CH_2CH_2$), 13.47 (CH_3). ^{11}B{^{1}H} NMR (DMSO-d_6, ppm): −3.78 (1 B, *B*N), −16.01 (11 B, *B*H). IR (KBr, cm^{-1}): 3187 (w, ν (NH)), 2964, 2876 (m, CH_2, CH_3)), 2488 (s, ν (BH)), 1572 (m, ν (C═C_{Ar})). MS (ESI) negative, *m*/*z*: 234 (A^-), 710 (2 A^- + $N(n\text{-}C_4H_9)_4^+$), positive: 242 ($N(n\text{-}C_4H_9)_4^+$). M.p.: 138 °C.

3.5. $[N(n\text{-}C_4H_9)_4]$[*closo*-$B_{12}H_{11}N(CH_3)_2C_6H_5$] (**7**)

0.50 g (0.80 mmol) of **5** was stirred and refluxed with 1.8 ml (0.0143 mol) *N*,*N*-dimethylaniline (bp. 193 °C) for 1 h, cooled, stirred in diethylether and filtered. The white powder was extracted with dichloromethane and diluted hydrochloric acid. The organic phase was dried over sodium sulphate. Dichloromethane was removed and the residue stirred overnight in a small amount of methanol. The colorless product **7** was filtered and dried.

Yield: 0.11 g (0.22 mmol, 28%). ^{1}H NMR (DMSO-d_6, ppm): 7.53 (d, 2H, NCH_{Ar}), 7.38 (t, 2H, CH_{Ar}), 7.28 (t, 1H, CH_{Ar}), 3.31 (s, 6H, CH_3), 3.08 (m, 8H, N-CH_2), 1.60 (m, 8H, N-CH_2CH_2), 1.35 (st, 8H, N-$CH_2CH_2CH_2$), 0.97 (t, 12H, CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm): 150.41 ($C_{Ar}N$), 128.08 ($C_{Ar}H$), 126.74 ($C_{Ar}H$), 121.83 ($C_{Ar}HCN$),

57.51 (NCH_2), 56.01 (NCH_3), 23.05 (NCH_2CH_2), 19.21 ($NCH_2CH_2CH_2$), 13.50 (CH_2CH_3). $^{11}B\{^1H\}$ NMR (DMSO-d_6, ppm): 3.26 (1 B, *B*N), −16.07 (11 B, *B*H). IR (KBr, cm^{-1}): 2960, 2874 (m, ν (CH_2, CH_3)), 2487 (s, ν (BH)), 1490 (m, ν (C=C)), 840 (w, ν (C=C)). MS (ESI) negative, *m*/*z*: 262, (A^-), 766 (2 A^- + $N(n\text{-}C_4H_9)_4^+$), positive: 242 ($N(n\text{-}C_4H_9)_4^+$). M.p.: 184 °C.

3.6. Preparation of Cs[1-closo-($B_{12}H_{11}NC_5H_4$)-4-$N(CH_3)_2$] (**8**)

0.50 g (0.80 mmol) of **5** was stirred and refluxed with 1.74 g (0.0142 mol) 4-(dimethylamino)pyridine to 200 °C for 2 h, cooled, stirred in diethylether and decanted. It was dissolved in dichloromethane and the insoluble residue was centrifuged. The solvent was removed and the brown residue was dissolved in methanol. 0.10 g (0.65 mmol) cesium fluoride was dissolved in a minimal amount of methanol and added. The colorless powder was centrifuged. To remove the reactant hot acetone was added to the solid and filtered hot. The acetone was removed and an oily residue remained which was stirred in diethylether to yield a colorless solid (**8**).

Yield: 0.05 g (0.12 mmol, 16%). ^1H NMR (DMSO-d_6, ppm): 8.18 (d, 2H, CH_{Ar}), 6.79 (d, 2H, CH_{Ar}), 3.06 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): 155.30 (NC_{Ar}), 144.02 ($CH_{Ar}N$), 106.50 (NC_{Ar}-$C_{Ar}H$), 38.97 (NCH_3). $^{11}B\{^1H\}$ NMR (DMSO-d_6, ppm): −1.52 (1 B, *B*N), −15.45 (11 B, *B*H). IR (KBr, cm^{-1}): 2951 (w, ν (CH_3)), 2488 (s, ν (BH)), 1731, 1645 (s, ν (C=C)). MS (ESI) negative, *m*/*z*: 263 (A^-), positive: 133 (Cs^+), 179 ($Me_2NC_5H_4NBu^+$). M.p.: >250 °C.

4. Conclusion

Two methods for the preparation of a boron–nitrogen–aryl linkage starting from dodecahydro-*closo*-dodecaborate and ammonioundecahydro-*closo*-dodecaborate, respectively, are described. Reactions of $[N(n\text{-}C_4H_9)]_2B_{12}H_{12}$ with arylamines such as aniline and *N*,*N*-dimethylaniline lead to the expected aryl ammonio derivatives of the cluster. Mass spectral analyses helped to explain the probable mechanistic pathway: in the case of *N*,*N*-dimethylaniline, and 4-(dimethylamino)pyridine, Hofmann elimination of the tetrabutylammonium ion at high temperatures takes place, initiated by the abstraction of a hydride from the cluster. The resulting electrophilic boron atom is attacked nucleophilicly by the amino nitrogen and the pyridine nitrogen atom, respectively. In the case of aniline and 4-aminopyridine, the formed hydride reacts with a proton of the amino group to form dihydrogen. The nucleophilic attack at the electropositive boron atom occurs by the amino nitrogen. These could also be the mechanisms of the reactions resulting in a linkage to nitrogen [11,12], or carbon [9], both described by Preetz et al.

Further investigations will find out if this kind of synthesis might be possible for a variety of nucleophiles provided that the boiling point is high enough so that a Hofmann elimination of the tetrabutylammonium cation and simultaneous formation of a positively charged boron atom can occur.

The nucleophilic aromatic substitution with $[closo\text{-}B_{12}H_{11}NH_2]^{2-}$ on aromatic systems with electron withdrawing substituents, such as 4-nitrophthalonitrile and 1-chloro-2,4-dinitrobenzene was successful. There are different possibilities for a substitution: elimination of halides, nitro groups and also a nucleophilic attack on the carbon with the highest partial positive charge and least steric hindrance is possible.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.053.

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