

Synthesis and X-ray structural characterisation of the tetramethylene oxonium derivative of the hydrodecaborate anion. A versatile route for derivative chemistry of $[B_{10}H_{10}]^{2-}$ ☆

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Abstract

The oxonium derivative $P(C_6H_5)_4[2-B_{10}H_9O(CH_2)_4]$ (**1**) has been prepared from $[B_{10}H_{10}]^{2-}$ by a solvent-addition reaction route, promoted by $Et_2O \cdot BF_3$. Its structure has been confirmed by single crystal X-ray analysis. **1** is assumed to be a useful synthon for the derivative chemistry of $[B_{10}H_{10}]^{2-}$. As an illustration, ring-opening reaction occurred in presence of the strong nucleophilic agent OH^- , giving the monoanionic derivative $[P(C_6H_5)_4]_2[2-B_{10}H_9O(CH_2)_4OH]$ (**2**).

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1. Introduction

The decahydro-*closo*-decaborate dianion $[B_{10}H_{10}]^{2-}$, as an element of the 10–12-vertex boron hydrides serie, occupies a unique position in inorganic cluster chemistry, mainly due, first, to its noteworthy thermal and chemical stability which can be related to its 3D electron delocalisation. Second, the presence of two different kinds of boron atoms within the cage, namely apical and equatorial positions, provides additional kind of reactivity compared to $[B_{12}H_{12}]^{2-}$. Various applications can be envisaged for the substitution derivatives of this cluster, the two main are the following: (i) target deriv-

atives for boron neutron capture therapy (BNCT), a method for treatment of cancer based upon the interaction of ^{10}B atoms and thermal neutron [1–3] and (ii) anionic extractants for the purification of nuclear wastes arising from PUREX process [4–6].

The chemistry of $[B_{10}H_{10}]^{2-}$ has been first developed in the 1960s, see e.g. [7,8], but has recently received much attention again. In a general way, this chemistry is much less investigated than the one of its analogue $[B_{12}H_{12}]^{2-}$. Several routes to substituted *closo*-decaborate anions can be envisaged: (i) the formation of *exo* boron–carbon bonds has been reviewed by Gabel et al. [1], (ii) the substitution reactions of the azonium derivative $[1-N_2B_{10}H_9]^+$ by amines, nitriles or phosphines have been reported by our group [4,5], (iii) the synthesis of the carbonyl derivative $[2-B_{10}H_9CO]^{2-}$ and its subsequent chemistry have been reported by Hawthorne and co-workers [9], (iv) the formation of carboxylic derivatives $[2-B_{10}H_9OC(O)R]^{2-}$ has been described [10,11] and (v) the chemistry of $[2-B_{10}H_9NH_3]^{2-}$ has been recently

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re-investigated [2]. To summarise, acid-catalysed substitution reactions are well known to lead to various derivatives but these reactions are difficult to control and may yield to mono- and/or poly-substituted compounds and then to mixture of isomers, which are difficult to separate [9]. In this context, the discovery of a simple and versatile route to derivative chemistry of $[\text{B}_{10}\text{H}_{10}]^{2-}$ is still an important scientific challenge. For that purpose, our idea was to transpose the useful general procedure developed notably by Plešek et al. [12,13] on the cobaltabis(dicarbollide) ions, by Sivaev et al. [14] on the dodecahydro-*closo*-dodecaborate anion $[\text{B}_{12}\text{H}_{12}]^{2-}$ and by Hawthorne and coworkers [15] on $[\text{B}_{20}\text{H}_{18}]^{2-}$. It consists in the formation of an oxonium derivative by reaction of the corresponding boron cluster with THF or dioxane. In a second step, the subsequent ring-cleavage reaction of the bonded heterocycle by almost any nucleophilic reactants (Z) can yield $[\text{cluster-O}(\text{CH}_2)_4\text{-Z}]^{n-}$ -like derivatives, as illustrated for instance with $[\text{B}_{12}\text{H}_{11}\text{O}(\text{CH}_2)_5]^-$ [16].

2. Results and discussion

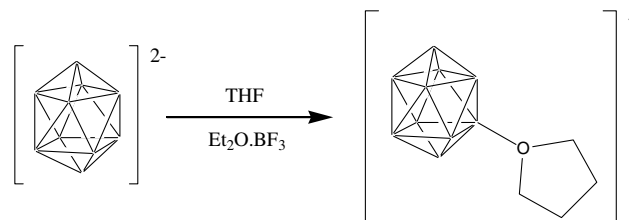
2.1. Synthesis of the $\text{P}(\text{C}_6\text{H}_5)_4[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ (**1**)

The synthesis of the title compound was conducted by dropwise addition of a small excess of boron trifluoride etherate, $\text{Et}_2\text{O} \cdot \text{BF}_3$, to a stirred slurry of $\text{K}_2[\text{B}_{10}\text{H}_{10}]$ in tetrahydrofuran (THF). After 2 days of stirring at room temperature, a precipitate was filtered off and a pale yellow solution was collected. The precipitate was analysed by ^1H and ^{11}B NMR and characterised as pure unreacted $\text{K}_2[\text{B}_{10}\text{H}_{10}]$. The filtrate was dried under vacuum yielding a white powder. The main product was isolated by chromatography on silicagel. It was first analysed by ^{11}B NMR spectroscopy, which is the simplest way to determine the degree of substitution of the cage. Indeed, the starting cluster, $[\text{B}_{10}\text{H}_{10}]^{2-}$, is featured by a “2 8” pattern, corresponding to the two boron atoms in the apical position (−1.22 ppm) and to the eight others in equatorial position (−30.29 ppm), respectively. The ^{11}B NMR spectrum of the resulting product is featured by a “1 1 1 2 2 2 1” pattern, which is characteristic of a *closo*-decaborate anion monosubstituted in the equatorial position, $[2\text{-RB}_{10}\text{H}_9]^{n-}$, see e.g. [10]. Each apical boron atom gives indeed one signal, the four boron atoms of the substituted crown and the four boron atoms of the second crown are featured by three signals and two signals, respectively. Moreover, the broad singlet at 2.8 ppm is the only one to be unaffected by proton coupling during the ^{11}B NMR analysis. This signal is thus attributed to the boron atom bearing the substituent group. The identification of this pendant group was conducted by ^1H NMR analysis. Beside the broad and unresolved signals (1.7–0.2 ppm) characteris-

tic of the hydrogen atoms linked to the cluster and the multiplet (8.0–7.5 ppm) featured the tetraphenylphosphonium anion, two signals were observed at 4.23 and 1.98 ppm. These two signals correspond to the two distinguishable methylene functions of the tetrahydrofuran ring in ortho- and meta-position vs. the oxygen atom, respectively. These values are slightly shifted compared to free THF (3.72 and 1.84 ppm) but are close to those reported by Sivaev et al. [14] for the tetramethylene oxonium derivative of the *closo*-dodecaborate anion (4.38 and 2.07 ppm). Moreover, the relative intensity of the different signals confirms the monoanionic nature of the product with only one tetraphenylphosphonium cation for one cluster and for one oxonium ring. Therefore, the ^1H NMR analysis permits to conclude that the product obtained is the tetramethylene oxonium derivative of the *closo*-decaborate, $\text{P}(\text{C}_6\text{H}_5)_4[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ (**1**). Therefore, the addition reaction of THF on $[\text{B}_{10}\text{H}_{10}]^{2-}$ occurs in presence of $\text{Et}_2\text{O} \cdot \text{BF}_3$ (Scheme 1).

We assume that the mechanism of this substitution reaction is similar in principle to that described for the THF substitution of $[\text{B}_{12}\text{H}_{12}]^{2-}$ [14] or for the carboxylic substitution of $[\text{B}_{10}\text{H}_{10}]^{2-}$ [11]. Boron trifluoride etherate acts as Lewis acid and promotes a substitution reaction by a polar solvent molecule. This reaction can thus be classified into the “acid-catalysed nucleophilic substitution” reactions, well known since the 1960s, see e.g. [7,8]. This assumption is confirmed by the equatorial position of the THF group, which is one of their main feature.

It is interesting to notice that the yield of this substitution reaction is quite low (40%) but this has to be counterbalanced by the fact that most of the expensive unreacted $\text{K}_2[\text{B}_{10}\text{H}_{10}]$ can be recovered after the filtration step. Only a few percent of cluster is lost due presumably to opening reaction of the oxonium ring, as it will be proposed below, with traces of nucleophilic reactants present in the THF solution. The co-products formed by these ring-opening reactions were separated from (**1**) during the chromatography step but their amounts were too low for any kind of chemical analysis. Beside these co-products, different experiments have been conducted in order to improve the yield of the substitution reaction. When adding a higher proportion of



Scheme 1.

boron trifluoride etherate, a waxy product is collected from which it was technically impossible to separate **1**.

2.2. X-ray structural determination of (**1**)

Single crystals of (**1**) suitable for X-ray diffraction were grown from a $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) solution. The crystallographic data have been summarised in Table 1.

The compound crystallises in the orthorhombic *Ama2* group with four molecules in the cell. Both anion and $\text{P}(\text{C}_6\text{H}_5)_4$ are situated around symmetry elements. Each phosphorous atom lying on a twofold axis, two phenyl groups were determined, the two axis giving the two other groups. Concerning the anion, a symmetry plane built from B3, B8 and B9 atoms was found in the cage (Fig. 1). There are thus two positions for the other boron atoms and this disorder affects the accuracy of the structure. Solution and refinement were calculated with SHELX programs [17]. Hydrogen atoms were assigned using the isotropic thermal parameters values based on those corresponding to the attached atoms. Refinement leads to *R* value of 0.0578, the largest peak on the electron map density being $0.236 \text{ e}\text{\AA}^{-3}$. Drawings were calculated by PLATON [18]. Fig. 1(a) and (b) give a view of the cation and substituted cluster, respectively, with the numbering scheme. Fig. 2 shows the disordered anion in the stereo mode.

The phenyl rings in $\text{P}(\text{C}_6\text{H}_5)_4$ have regular geometry and the structural parameters of this cation are classical. The distances $\text{P}(1)\text{C}(1)$ and $\text{P}(1)\text{C}(7)$ are 1.796(3) and 1.792(2) Å, respectively. The angle $\text{C}(1)\text{P}(1)\text{C}(7)$ is $111.4(2)^\circ$.

The geometry of the anion can be described as a slightly distorted bicapped square antiprism, exhibiting a deviation from the ideal polyhedron. Apical–equatorial distances vary from 1.36 to 1.76 Å with a mean value of 1.63 Å, while the equatorial–equatorial ones vary from 1.73 to 2.37 Å with a mean value of 1.79 Å. These mean values are in good agreement with those reported by other authors for equatorially monosubstituted derivative [2,9,10,19–21] or for non-substituted

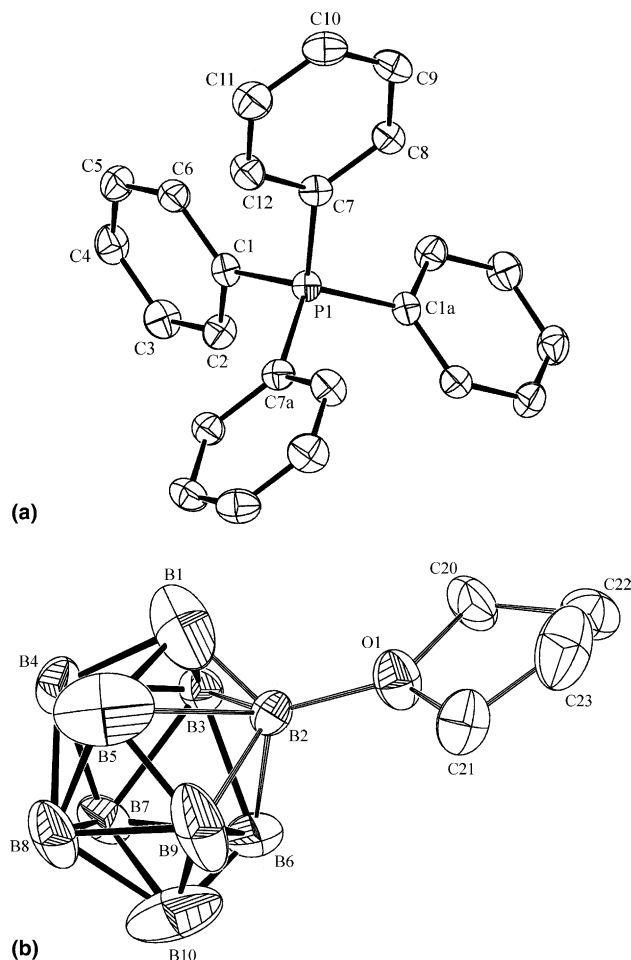


Fig. 1. ORTEP drawings of $\text{P}(\text{C}_6\text{H}_5)_4$ (a) and substituted cluster **1** (b) showing the atom-numbering scheme. Selected bond distances (Å) and angles ($^\circ$): $\text{B}(2)\text{O}(1)$, 1.522(9); $\text{B}(1)\text{B}(3)$, 1.716(8); $\text{B}(2)\text{B}(3)$, 1.799(9); $\text{B}(3)\text{B}(4)$, 1.798(7) $\text{B}(2)\text{O}(1)\text{C}(20)$, $118.9(7)$; $\text{B}(2)\text{O}(1)\text{C}(21)$, $131.0(7)$

Table 1

Crystallographic data for $\text{P}(\text{C}_6\text{H}_5)_4[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ (**1**)

Formula	$\text{C}_{28}\text{H}_{37}\text{B}_{10}\text{O}_1\text{P}_1$
<i>M</i> (g mol^{-1})	519.58
Temperature (K)	293(2)
Space group	<i>Ama2</i>
<i>a</i> (Å)	22.407(5)
<i>b</i> (Å)	17.373(4)
<i>c</i> (Å)	7.5626(15)
<i>V</i> (Å ³)	2944.0(10)
<i>Z</i>	4
ρ_{calc} (g cm^{-3})	1.172
μ (mm^{-1})	0.115
Refinement method	Full-matrix least-squares on F^2
<i>R</i> , <i>R</i> _w , GOF	0.0578, 0.1628, 1.050

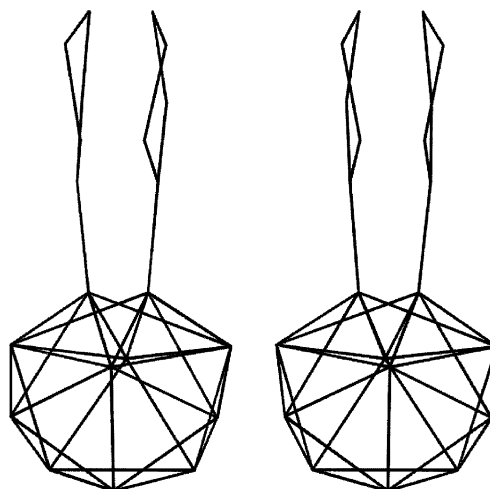
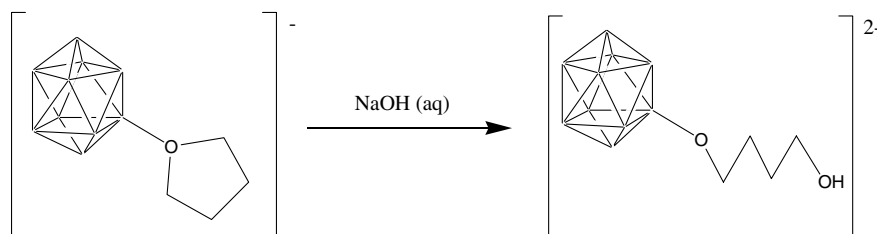


Fig. 2. Drawing of the disordered anion in the stereo mode.



Scheme 2.

closo-decaborate [22,23]. The $\text{exo B}_{\text{eq}}\text{--O}$ distance (1.522 Å) is significantly longer than those reported for $[\text{Pb}(\text{bipy})(\text{DMF})(\text{B}_{10}\text{H}_9\text{OH})]\cdot\text{DMF}$ (1.47 Å) [10] and for the hydroxy-*closo*-dodecaborate (1.426 Å) [24]. The angle between $\text{O}(1)\text{B}(2)$ bond and $\text{B}(2)\text{B}(1)$, $\text{B}(2)\text{B}(5)$, $\text{B}(2)\text{B}(3)$ and $\text{B}(2)\text{B}(9)$ bonds are $81.9(4)^\circ$, $134.4(5)^\circ$, $129.2(6)^\circ$ and $118.3(6)^\circ$, respectively.

2.3. Ring-opening reaction, synthesis of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4\text{OH}]$ (**2**)

As it is mentioned above, (**1**) can be envisaged as a useful synthon for the derivative chemistry of the *closo*-decaborate anion. For that purpose and in order to parallel the works developed on other boron clusters, a ring-opening reaction has been investigated. Therefore a slurry of (**1**) into an aqueous sodium hydroxide solution was stirred overnight. As expected from the results obtained with other clusters [12–16], a ring-opening reaction has occurred (Scheme 2).

As expected, the attack of a strong nucleophilic agent, namely OH^- , onto the carbon in α -position on the oxonium ring resulted in the cleavage of the carbon–oxygen bond, yielding $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4\text{OH}]$ (**2**). Unreacted **1** was filtered off and dianion **2**, which is soluble in water, can be precipitate as its tetraphenylphosphonium salt. The ^{11}B NMR spectrum of $[\text{P}(\text{C}_6\text{H}_5)_4]_2$ (**2**) is similar to that of $[\text{P}(\text{C}_6\text{H}_5)_4]$ (**1**). The broad singlet of the boron atom bearing the pendant group is shifted downfield (−0.4 ppm). The ^1H NMR spectrum shows the splitting of the methylene group into three signals at 3.3, 3.1 and 1.4 ppm attributed to the $-\text{CH}_2\text{--OB}$, to the terminal $-\text{CH}_2\text{--OH}$ and the central $-\text{CH}_2\text{--}$ groups, respectively. The relative intensity of the different signals is consistent with the dianionic nature of compound **2**. The yield is almost low (50%) but the unreacted oxonium derivative **1** is fully recovered by filtration.

3. Experimental

3.1. Starting materials and instruments

All sensitive compounds were handled under atmosphere of pure argon using vacuum-line, Schlenk techniques and an efficient dry box with solvents purified

by standard methods [25]. $(\text{Et}_3\text{HN})_2[\text{B}_{10}\text{H}_{10}]$ was provided by KATCHEM Ltd., Prague (Czech Republic). ^{11}B and ^1H NMR spectra were recorded on a Brüker AM 300 spectrometer in CDCl_3 or CD_3CN at 96.29 MHz with $\text{Et}_2\text{O}\cdot\text{BF}_3$ as external reference (positive values downfield) and at 300 MHz, respectively. The following abbreviations are used: s, singlet, d, doublet, m, multiplet, u, unresolved signal. The infrared spectra were recorded on a FTIR Nicolet Magna 550 spectrometer as Nujol mulls between CsI plates in a hermetic cell or as KBr pellets. Single crystal diffraction data were collected using a Nonius KappaCCD diffractometer. Details of the data collection and structure refinement can be found in Table 1.

3.2. Synthesis of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ (**1**)

$(\text{Et}_3\text{HN})_2[\text{B}_{10}\text{H}_{10}]$ was converted to $\text{K}_2[\text{B}_{10}\text{H}_{10}]$ by passing on a C20 H Duolite resin charged with protons followed by neutralisation with potassium hydroxide. In a typical experiment, 5.8 mmol (0.82 g, 0.73 ml) of boron trifluoride etherate, $\text{Et}_2\text{O}\cdot\text{BF}_3$, was slowly added dropwise at room temperature to a slurry of $\text{K}_2[\text{B}_{10}\text{H}_{10}]$ (0.95 g, 4.84 mmol) in 50 ml of fresh distilled tetrahydrofuran (THF). The reaction mixture was kept under stirring at room temperature for 2 days. The unreacted decahydro-*closo*-decaborate anion was subsequently filtrated off yielding a pale yellow solution. The filtrate was dried in vacuo in order to remove traces of solvent. The ensuing white powder was dissolved in water (50 ml) and crude product, containing mainly the title compound, was precipitated as tetraphenylphosphonium salts by addition of a large excess of tetraphenylphosphonium bromide, $\text{BrP}(\text{C}_6\text{H}_5)_4$. Further purification was performed by chromatography on silicagel (NORMASIC 40–60 μm , Aldrich) using a $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) solution and yields, after evaporation of the solvent in vacuo, 1.02 g (1.94 mmol) of pure $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ (**1**), (yield 40%). Single crystals of **1** were obtained from a $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) solution by a slow evaporation of the solvent mixture at room temperature.

FTIR (KBr pellets, cm^{-1}): 3057, 2958–2872, 2478–2439, 1579, 1476, 1437, 1108, 922, 724, 689.

$^{11}\text{B}\{^1\text{H}\}$ NMR (δ , ppm, CH_3CN): 2.8 (s, 1B), −1.3 (s, 1B), −7.8 (s, 1B), −24.0 (s, 2B), −25.6 (s, 2B), −31.8 (s, 2B), −32.9 (s, 1B).

^1H NMR (δ , ppm, CDCl_3): 8.0–7.5 (m, 20H C_6H_5), 4.23 (t, 4H, $-\text{O}(\text{CH}_2\text{CH}_2)_2$), 1.98 (m, 4H, $-\text{O}(\text{CH}_2\text{CH}_2)_2$), 1.7–0.2 (u, 9H BH).

Elemental Analysis for (1). Calc.: B, 20.4; C, 63.6; H, 7.0. Found: B, 19.5; C 62.0; H, 6.9% [26].

3.3. Synthesis of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4\text{OH}]$ (2)

A slurry of 0.192 g (0.36 mmol) of $\text{P}(\text{C}_6\text{H}_5)_4[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ into 100 ml of a 2 M solution of sodium hydroxide was stirred at room temperature overnight. Unreacted 1 was filtered off and the solution was neutralised by 2 M aqueous HCl. The solution was passed on a C20 H Duolite resin charged with protons followed by neutralisation with potassium hydroxide. The title compound was precipitated as tetraphenylphosphonium salts by addition of a large excess of tetraphenylphosphonium bromide. Further recrystallisation in CH_3CN gives 0.159 g (0.18 mmol, 50%) of pure $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4\text{OH}]$, $[\text{P}(\text{C}_6\text{H}_5)_4]_2$ (2).

FTIR (KBr pellets, cm^{-1}): 3053, 2919, 2837, 2487, 2435, 1584, 1480, 1441, 1104, 715, 689.

$^{11}\text{B}\{^1\text{H}\}$ NMR (δ , ppm, CH_3CN): -0.4 (s, 1B), -2.5 (s, 1B), -5.0 (s, 1B), -23.3 (s, 4B), -28.9 (s, 2B), -33.4 (s, 1B).

^1H NMR (δ , ppm, CD_3CN): 8.0–7.5 (m, 40H C_6H_5), 5.0 (s, 1H, OH), 3.3 (u, 2H, $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)$), 3.1 (u, 2H, $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)$), 1.4 (u, 4H, $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)$), 1.1–1.0 (u, 9H BH).

Elemental Analysis for (2). Calc.: B, 12.2; C, 70.6; H, 6.5. Found: B, 11.7; C 68.2; H, 6.5% [26].

4. Conclusion

A useful synthon $\text{P}(\text{C}_6\text{H}_5)_4[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4]$ has been prepared from $[\text{B}_{10}\text{H}_{10}]^{2-}$ by a solvent-addition reaction promoted by $\text{Et}_2\text{O} \cdot \text{BF}_3$. This compound has been fully characterised by NMR and its structure has been confirmed by single crystal X-ray diffraction analysis. A ring-opening reaction by hydroxide anion, acting as a strong nucleophilic agent, was observed yielding the dianion $[\text{P}(\text{C}_6\text{H}_5)_4]_2[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2)_4\text{OH}]$. The authors assume that this route is suitable for the versatile derivative chemistry of $[\text{B}_{10}\text{H}_{10}]^{2-}$ and further experiments are conducted in order to prepare various derivatives of this cluster.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 235095 for compound 1. Elemental analyses were obtained from the Service Central d'Analyses du CNRS (Solaize, France).

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