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Synthesis and X-ray structural characterization of the triphenylphosphine derivative of the *closo*-dodecaborate anion, *closo*-[1-$B_{12}H_{11}P(C_6H_5)_3$][$N(n\text{-}C_4H_9)_4$]

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Abstract

The reaction of a molar excess of *closo*-[$B_{12}H_{11}I$][$N(n\text{-}C_4H_9)_4$]$_2$ (**1**) with tetrakis(triphenylphosphine)palladium (0), $Pd(0)L_4$, yields to the formation of the title monoanionic compound, *closo*-[1-$B_{12}H_{11}P(C_6H_5)_3$][$N(n\text{-}C_4H_9)_4$] (**2**). The structure of **2** was determined by X-ray diffraction analysis performed on a single crystal. The mechanism of formation of **2** is also discussed. We suggested a two-step mechanism for the formation of **2** consisting in a oxidative addition of the palladium complex followed by a reductive elimination involving $P(C_6H_5)_3$ and assisted by Na_2CO_3. To our knowledge, this is the first example of monosubstitution of B_{12} with formation of boron–phosphorus bond.

Keywords: Dodecahydro-*closo*-dodecaborate; Boron cluster; Phosphine derivative; Palladium catalysis

1. Introduction

The dodecahydro-*closo*-dodecaborate dianion, [$B_{12}H_{12}$]$^{2-}$, possesses the structure of a regular icosahedron and unique properties, such as high thermal stability, remarkable chemical and hydrolytical stability and a low toxicity. Since the isolation of *closo*-[$B_{12}H_{12}$]$^{2-}$ has been first reported in 1960 [1], several routes to substituted *closo*-dodecaborate anions were envisaged via the formation of boron–nitrogen [2–4], –oxygen [5–8], –sulfur [9,10], –halogen [11–13], or –carbon [14–16] bonds. Their intrinsic properties make B_{12}-derivatives suitable for various possible applications, ranging from biomedical ones like boron neutron capture therapy (BNCT), a method for treatment of cancer based upon the interaction of ^{10}B atoms and thermal neutron [16–18], to the selective extraction of radionuclides from nuclear wastes arising from PUREX process [19–21]. The chemistry of *closo*-[$B_{12}H_{12}$]$^{2-}$, together with the potential applications of its derivatives, was reviewed by Sivaev et al. in 2002 [22].

In the present study, our attention was focused on the functionalization of *closo*-[$B_{12}H_{12}$]$^{2-}$ through the formation of boron–phosphorus bonds. Only few examples of *closo*-dodecaborate substituted by phosphorus derivatives have been reported in the literature. In the early 1960s, when examinating new efficient routes for the preparation of [$B_{12}H_{12}$]$^{2-}$, Miller et al. [23,24] have shown that the reaction of diborane, B_2H_6, with trimethylphosphine–borane complex, $(CH_3)_3PBH_3$, affords the formation of the monoanion *closo*-[$B_{12}H_{11}P(CH_3)_3$]$^-$ (60% yield) (Scheme 1), with neutral *closo*-[$B_{12}H_{11}$-$(P(CH_3)_3)_2$] as a by-product (5% yield).

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$$2\,(CH_3)_3PBH_3 \;+\; 5\,B_2H_6 \xrightarrow{175\ ^\circ C} [B_{12}H_{11}P(CH_3)_3]^- \;+\; 11\,H_2$$

Scheme 1.

$$[B_{12}H_{12}]Li_2 \;+\; (PMe_2Ph)_2PdCl_2 \xrightarrow{THF} (PMe_2Ph)_2B_{12}H_{10} \;+\; 2\,LiCl \;+\; [L_nPd]$$

Scheme 2.

More recently, Todd and co-workers [25] have shown that the reaction of $[B_{12}H_{12}]Li_2$ with $(PMe_2Ph)_2PdCl_2$ yields the charged-compensated dodecaborate cluster $(PMe_2Ph)_2B_{12}H_{10}$ (Scheme 2).

Starting from the monoiodo derivative $[B_{12}H_{11}I]^{2-}$, we describe in this report a synthetic method for palladium-assisted monosubstitution of B_{12} by phosphine group, along with the X-ray structure of *closo*-[1-$B_{12}H_{11}P(C_6H_5)_3$][N(*n*-$C_4H_9)_4$].

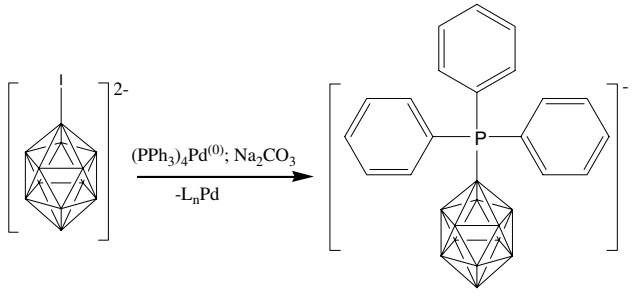
2. Results and discussion

2.1. Synthesis of $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (2)

As we found, starting from the well-known monoiodo derivative *closo*-$[B_{12}H_{11}I][N(n\text{-}C_4H_9)_4]_2$ (**1**), the synthesis of the title compound was conducted by addition of an excess of **1** to tetrakis(triphenylphosphine)palladium, L_4Pd. After 72 h of stirring at 50 °C and a subsequent elimination of the residual Pd-based species by filtration through a pad of celite, $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (**2**) was separated from unreacted **1** by chromatography on silicagel. This product was first analyzed by ^{11}B NMR spectroscopy, which is the simplest method to determine the degree substitution of the boron cluster. Its ^{11}B NMR spectrum is featured by a "1 5 5 1" pattern, characteristic of a monosubstituted *closo*-dodecaborate. The singlet at −8.4 ppm was attributed to the boron atom in the apical position, while the two singlets at −12.3 and −13.5 ppm were attributed to boron atoms in equatorial position. The signal at −17.9 ppm, corresponding to the boron atom bearing the triphenylphosphine group, appears as a doublet due to the coupling with the phosphorus atom (J_{B-P} = 134 Hz). These data are consistent with those reported by Todd and co-workers [25] concerning the charge-compensated cluster 1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$. Consistently, the ^{31}P NMR spectrum of **2** shows only one quartet centered at 6.8 ppm. The structure of **2** was undoubtedly confirmed by ^1H NMR analysis. Beside the broad and unresolved signals (2.5–0.5 ppm) characteristic of the hydrogen atoms linked to the cluster and the four multiplets centered at 0.9, 1.3, 1.6, and 3.2 ppm corresponding to the methyl and to the tree methylene groups featured the tetrabutylammonium cation, three multiplets were observed at 7.7, 7.5, and 7.4 ppm. These multiplets were attributed to the phenyl hydrogen atoms of the triphenylphosphine pendant group. These data are in good agreement with those reported for 1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$ [25]. It is interesting to notice that the chemical shifts measured for the phenyl hydrogen atoms of **2** are shifted compared to those of triphenylphosphine (7.1–7.9 ppm) and closer to those of tetraphenylphosphonium bromide (7.6–7.9 ppm), the phosphorus atom of **2** being tetravalent. Moreover the relative intensity of the different signals in the ^1H NMR spectrum of **2** confirms the monoanionic nature of the product with only one tetrabutylammonium cation for one cluster and one triphenylphosphine group. Therefore, the reaction of a molar excess of *closo*-$[B_{12}H_{11}I][N(n\text{-}C_4H_9)_4]_2$ (**1**) with tetrakis(triphenylphosphine)palladium (0) yields to the formation of *closo*-[1-$B_{12}H_{11}P(C_6H_5)_3$][N(*n*-$C_4H_9)_4$] (**2**) (Scheme 3).

During this substitution reaction, the fate of the palladium (0) is not completely understood which was emphasized by the presence of product $[L_nPd]$ in Scheme 3. We assume a two-step mechanism for the formation of **2**. First is an oxidative addition of $[B_{12}H_{11}I]^{2-}$ on the reactive palladium (0) complex, PdL_2 (L = PPh_3) which yields to the formation of an anionic intermediate in the catalytic cycle (Scheme 4), as reported by Hawthorne and co-workers [26] during the palladium-catalyzed coupling of $[B_{12}H_{11}I]^{2-}$ with Grignard reagents. In the latter, the alkylation or arylation of B_{12} occurs in presence of the corresponding Grignard reagents.

We have no experimental evidence concerning the second step of this process. We assume that, in our case i.e., in absence of Grignard reagents, this second-step is a reductive elimination step involving triphenylphosphine. Even if its role has not been fully understood, the presence of a base, Na_2CO_3, is necessary since



Scheme 3.

$$[B_{12}H_{11}I]^{2-} + [(PPh_3)_2Pd] \xrightarrow{THF} [B_{12}H_{11}\text{-}Pd(PPh_3)_2\text{-}I]^{2-}$$

Scheme 4.

$$[B_{12}H_{11}\text{-}Pd(PPh_3)_2\text{-}I]^{2-} \xrightarrow[-\ L_nPd^{(0)}]{THF,\ Na_2CO_3} [B_{12}H_{11}PPh_3]^{-}$$

Scheme 5.

experiment conducted without it did not permit to isolate **2** (Scheme 5).

For the preparation of neutral $(PMe_2Ph)_2B_{12}H_{10}$ from $[B_{12}H_{12}]^{2-}$, Todd and co-workers [25] have also suggested a two-step mechanism involving the formation of PdLBH four-centered intermediate. We assume that using the monoiodo derivative **1** as starting compound and palladium (0) complex as catalyst, instead of L_2Cl_2Pd (II), permit to preclude any direct reaction involving BH unit and yield selectively monosubstituted derivative.

2.2. X-ray structural determination of $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (2)

The solid-state structure of **2** was determined by X-ray diffraction analysis performed on a single crystal, grown at r.t. from a CH_3CN/CH_2Cl_2 (1:3) solution by a slow evaporation of the solvent mixture. The crystallographic data have been summarized in Table 1.

The compound **2** crystallizes in the monoclinic *P*2(1)/*n* group with four molecules in the cell. Fig. 1 gives a view of the cation and substituted cluster with the numbering scheme and selected values of bond distances and angles.

To our knowledge, this solid-state structure is the first example of monosubstituted B_{12} exhibiting a boron–phosphorus bond. The tetrabutylammonium cation has a regular geometry and the crystallographic parameters concerning this cation are fairly unexceptional. The

Table 1
Crystallographic data for $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (**2**)

Formula	$C_{34}H_{62}B_{12}N_1P_1$
F_w	645.54
Temperature (K)	160(2)
Space group	*P*2(1)/*n*
Unit cell dimensions	
a (Å)	10.103(10)
b (Å)	12.365(2)
c (Å)	31.168(4)
V (Å^3)	3861.28(9)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.110
μ (mm^{-1})	0.097
Refinement method	Full matrix least-squares on F^2
R, R_w, GOF	0.0651, 0.1591, 1.135

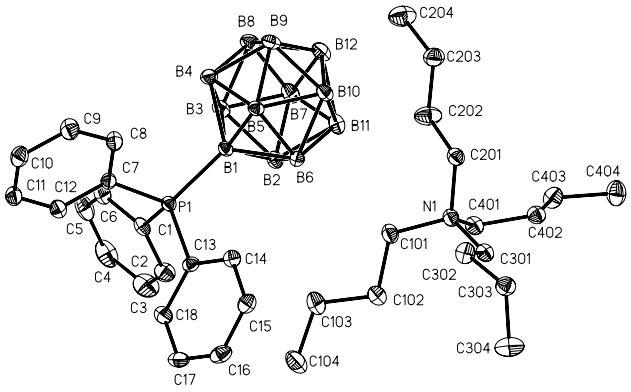


Fig. 1. ORTEP drawings of $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (**2**) showing the atom-numbering scheme. Selected bond distances (Å) and angles (°): B(1)–P(1), 1.928(2); B(1)–B(2), 1.784(3); B(2)–B(7), 1.788(3); B(7)–B(12), 1.783(4); P(1)–C(1), 1.811(2) and C(1)–P(1)–B(1), 109.13(9).

phenyl rings in $P(C_6H_5)_3$ have also a regular geometry with a phosphorus–carbon bond distance of 1.816 Å in average. Concerning the anion, the boron–boron bond distances vary in the range 1.76–1.96 Å. These values are in good agreement with those reported for similar monosubstituted B_{12} cluster [26,27]. The cage is not distorted by the presence of the phosphorus-based pendant group. The boron–phosphorus bond distance B(1)–P(1) is 1.928 Å. This value is consistent with those reported for 2,8-$(PMe_2Ph)_2$-$B_{10}H_8$ (1.894 Å) [25], [6-(PMe_2Ph)-*closo*-1-CB_9H_9] (1.90 Å) [28], and [2,2-$(PMe_3)_2$-2,1-closo-$PdTeB_{10}H_9(PPh_3)$] (1.96 Å) [29].

3. Experimental

3.1. General considerations

All reactions were carried out under atmosphere of pure argon using vacuum-line and schlenk techniques with solvents purified by standard methods [30]. $(Et_3NH)_2[B_{12}H_{12}]$ was purchased from KATCHEM Ltd., Prague, and used without further purification. ^1H, ^{11}B and ^{31}P NMR spectra were recorded on a Brüker AM 300 spectrometer in CD_2Cl_2 at 300 MHz, 96.29 MHz with $Et_2O \cdot BF_3$ as external reference (positive values downfield), and 146.2 MHz with 85% H_3PO_4 as external reference, respectively. The infrared spectra were recorded on a FTIR Nicolet Magna 550 spectrometer.

3.2. Synthesis of $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (2)

$(Et_3NH)_2B_{12}H_{12}$ was converted to $Na_2B_{12}H_{12}$ by passing on a C20 H Duolite resin charged with protons following by addition of sodium hydroxide. $Na_2B_{12}H_{12}$ was converted by reaction with iodine followed by precipitation with an excess of tetrabutylammonium

chloride into the monoiodo derivative *closo*-$[B_{12}H_{11}I][N(n\text{-}C_4H_9)_4]_2$ (**1**) as described in the literature [11].

Sodium carbonate, Na_2CO_3, (0.265 g, 2.5×10^{-3} mol) and tetrakis(triphenylphosphine)palladium (0), $(PPh_3)_4$-Pd, (0.155 g, 1.3×10^{-4} mol) was added at r.t. to a solution of an excess of **1** (0.751 g, 1.0×10^{-3} mol) in 20 mL of freshly distilled THF. The reaction mixture was subsequently heated up to 50 °C and stirred for 72 h at this temperature yielding a black suspension. The ensuing precipitate of [LnPd] was filtered off on celite bed. The solvent was evaporated in vacuum and $[B_{12}H_{11}P(C_6H_5)_3]N(n\text{-}C_4H_9)_4$ (**2**) was separated from unreacted **1** by chromatography on silicagel (NORMASIC 40–60 μm, Aldrich) using a CH_3CN/CH_2Cl_2 (1:3) solution (yield: 0.045 g, 7.0×10^{-5} mol, 54%).

^1H NMR (δ, ppm, $CDCl_3$): 7.7 (m, 6H, PC_6H_5), 7.5 (m, 3H, PC_6H_5), 7.4 (m, 6H, PC_6H_5), 3.2 (t, 8H, $N(CH_2(CH_2)_2CH_3)$), 1.6 (m, 8H, $N(CH_2CH_2CH_2CH_3)$), 1.3 (m, 8H, $N(CH_2CH_2CH_2CH_3)$), 0.9 (t, 12H, $N(CH_2CH_2CH_2CH_3)$), 2.5–0.5 (u, 11H, B*H*).

$^{11}B\{^1H\}$ NMR (δ, ppm, $CHCl_3$): −8.4 (s, 1B), −12.3 (s, 5B), −13.5 (s, 5B), −17.9 (d, J_{B-P} = 134 Hz, 1B).

$^{31}P\{^1H\}$ (δ, ppm, $CHCl_3$), 6.8 (q, J_{B-P} = 134 Hz).

FTIR (cm^{-1}): 3066; 2962; 2932; 2876; 2496; 1480; 1471; 1444; 1373; 1100; 1065; 1048; 745; 690.

3.3. X-ray structural determination of $[B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (2)

Single crystals of **2** were obtained from a CH_3CN/CH_2Cl_2 (1:3) solution by a slow evaporation of the solvent mixture. X-ray single-crystal diffraction data were collected at low temperature (160(2) K) using a Nonius KappaCCD diffractometer equipped with a normal monochromatized focus X-ray tube having a molybdenum target. The data were collected using the COLLECT software (Nonius BV, 1997–2000) and were then processed through the DENZO reduction software (Otwinoski & Minor, 1997). The structures were solved and refined on F^2 using the SHELXTL software [31]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated positions with isotropic thermal parameters. Crystal structure and refinement data are summarized in Table 1.

4. Conclusion

In this paper, we have investigated the reaction of *closo*-$[B_{12}H_{11}I][N(n\text{-}C_4H_9)_4]_2$ (**1**) with palladium (0) complex. The reaction pathway can be summarized as the replacement of the iodine atom by one of the ligand of the palladium complex. Indeed we have found that *closo*-$[1\text{-}B_{12}H_{11}P(C_6H_5)_3][N(n\text{-}C_4H_9)_4]$ (**2**) can be prepared by the reaction of a molar excess of **1** with tetrakis(triphenylphosphine)palladium (0). The structure of **2** was determined by X-ray diffraction analysis performed on a single crystal. We suggested a two-step mechanism for the formation of **2** consisting in a oxidative addition of the palladium complex followed by a reductive elimination involving $P(C_6H_5)_3$ and assisted by Na_2CO_3. To our knowledge, this is the first example of a monosubstitution reaction of B_{12} with formation of boron–phosphorus bond. We are now studying the monosubstitution of B_{12} by different phosphorus-based pendant group by varying the nature of the starting palladium (0) complex.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No. 254256 for compound **2**.

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