Synthesis and Characterization of the *nido*-Platinaborane $7,7\text{-}(PPh_3)_2\text{-}7\text{-}PtB_{10}H_{11}\text{-}11\text{-}OC(O)Me$

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Z. Naturforsch. **2011**, *66b,* 387 – 391; received December 15, 2010

The reaction of *closo*-$B_{10}H_{10}^{2-}$ with $PtCl_2(PPh_3)_2$ in the presence of MeCOSH afforded the title platinaborane *nido*-$7,7\text{-}(PPh_3)_2\text{-}7\text{-}PtB_{10}H_{11}\text{-}11\text{-}OC(O)Me$ (**1**), which has been characterized by IR and NMR spectroscopy, MS, elemental analysis, and single-crystal X-ray diffraction. In contrast to the known products having *exo*-polyhedral Pt-S-C-O-B ring(s) from the same reaction with PhCOSH, compound **1** has a *B*-acetoxy group on the open PtB_4 face of the *nido*-PtB_{10} cluster. The structure of **1** features both intramolecular/intermolecular C–H···O hydrogen bonds and intramolecular C–H···H–B dihydrogen bonds, which link the molecules into a 1-D chain structure.

Key words: Boron Cluster, Metallaborane, Platinaborane, Hydrogen Bond, Supramolecular Chemistry

Introduction

The reactions of the boranate anion *closo*-$B_{10}H_{10}^{2-}$ (Fig. 1) with $PtX_2(PR_3)_2$ (X = Cl, Br, I; R = alkyl or aryl groups) in different reaction media have been studied by several research groups [1 – 11]. Such reactions have been found to be sensitive to the conditions utilized and to afford in general platinaborane products *via* a polyhedral expansion process. Thus, when carried out in alcohols the reactions produce 11-vertex *nido*-7-platinaundecaboranes (Fig. 1) $[(PR_3)_2PtB_{10}H_{11}(OR')]$ or $[(PR_3)_2PtB_{10}H_{10}(OR')_2]$ (R′ = Me, Et, *i*Pr) with *B*-alkoxy substituent(s) [11]. However, exceptions are also known. Zheng *et al.* reported that from the reaction in *t*BuOH (reactant ratio $Pt : B_{10}H_{10}^{2-} = 1 : 2$, reflux for 120 h) a tetranuclear “triple cluster” $[(PPh_3)_2Pt_2B_{10}H_{10}(OtBu)]_2$ [7] was isolated from a mixture of products. We have recently repeated the same reaction in *t*BuOH (reactant ratio 1 : 1, reflux for 70 h) and obtained the partially chlorinated compound $[(PPh_3)_2PtB_{10}H_{10}\text{-}9,10\text{-}(H_{0.7}Cl_{0.3})_2]$ [12]. Recent progress in this direction has revealed that the same reactions in alcohols (EtOH, *i*PrOH) under solvothermal conditions give partially degraded diplatinaundecaboranes with a novel *nido*-$\{Pt_2B_9\}$ cluster core [1 – 4]. These interesting results indicate that new structures may be obtained by tuning the reaction conditions, which will in turn provide more information on the cage opening mechanism of *closo*-$B_{10}H_{10}^{2-}$ in the presence of transition metal complex(es).

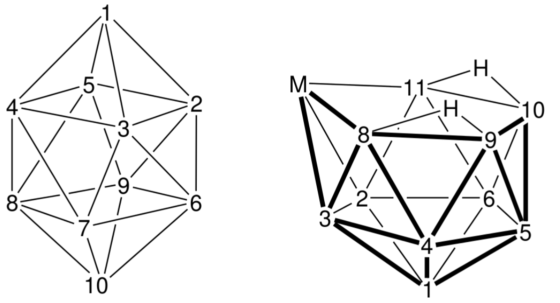


Fig. 1. Schematic representation and numbering of the *closo*-$B_{10}H_{10}^{2-}$ and *nido*-7-$MB_{10}H_{12}$ skeletons (each vertex with a number represents a BH unit).

It is believed that such reactions proceed *via* $\{PtB_{10}H_{10}\}$ intermediate(s) in which the Pt atom coordinates to the decaborate moiety *via* two hydrogen atoms [9 – 11]. The following attack on such intermediate(s) by alcohol or other reagents would then give the 11-vertex platinaborane product(s). Spectroscopic results [8] have shown that the possible alkoxy substitution can occur at 2-, 3-, 5-, 6-, 8-, 9-, 10-, or 11-positions at the $\{PtB_{10}\}$ cluster, however, the following experimental studies [1–7] revealed that the alkoxy substitutents may occupy various boron atoms of (for monoalkoxy substitution) 8-, 9-, 10-, 11-, or (for dialkoxy substitution) 8,10-, or 9,10-positions. In addition, while the same reactions in the presence of carboxylic acids (*e. g.* oxalic acid [8]) instead of alcohols did not afford any tractable metallaborane product, when $B_{10}H_{10}{}^{2-}$ was reacted with $PtCl_2(PPh_3)_2$ and PhCOSH, *nido*-PtB_{10} clusters featuring *exo*-polyhedral Pt-S-C-O-B cyclization were obtained [13. 14]. This is also true with the nickel complex $NiCl_2(PPh_3)_2$, which was reacted with $B_{10}H_{10}{}^{2-}$ and RCOSH (R = Ph, Me) to give the corresponding *nido*-nickelaundecaboranes with *exo*-polyhedral Ni-S-C-O-B ring(s) [15–20].

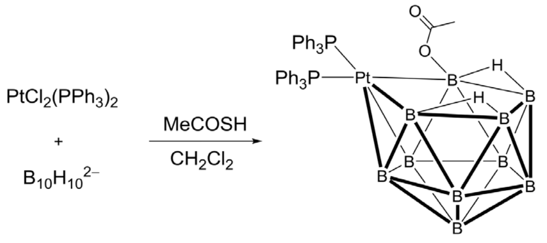
In order to get more information on the system of $B_{10}H_{10}{}^{2-}$ and $PtCl_2(PPh_3)_2$, we have investigated the reaction in the presence of MeCOSH and obtained the title compound $[(PPh_3)_2PtB_{10}H_{11}$-11-(OCOMe)] (**1**) which has a *B*-acetoxy group on the *nido*-PtB_{10} cluster, in much contrast to the known results mentioned above. Additionally, compound **1** exhibits a chain structure featuring both intramolecular/intermolecular C–H···O hydrogen bonds and intramolecular C–H···H–B dihydrogen bonds. Herein we report on the synthesis and structural characterization of **1**.

Results and Discussion

Synthesis and characterization of 1

We carried out the reaction of $B_{10}H_{10}{}^{2-}$ with $PtCl_2(PPh_3)_2$ in the presence of MeCOSH in refluxing CH_2Cl_2 and obtained, after TLC separation of a mixture of products, the platinaborane $[(PPh_3)_2PtB_{10}H_{11}$-11-(OOCMe)] (**1**) (Scheme 1), which was characterized by spectroscopic methods and elemental analysis. Its structure was further confirmed by a single-crystal X-ray diffraction study (see below).

The IR spectrum of **1** exhibits strong absorption peaks at 2541 and 1732 cm^{-1}, which can be assigned to the stretching of the B–H and C=O moieties, respectively. In the ^{11}B NMR spectrum, the typical pattern of a monosubstituted *nido*-PtB_{10} cluster is observed with eight partially overlapping resonance peaks indicating that the acetoxy substituent is fluxional over the boron atoms of the PtB_{10} cluster, as found in related *B*-alkoxy-substituted platinaboranes [8]. In addition, the HR-MS spectra and the elemental analysis clearly proved the composition of **1**.



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Scheme 1. Synthesis of compound **1**.

Mechanistic consideration of the formation of 1

Reactions as the one described here are usually complicated and afford a mixture of products, reflecting the complex cage-opening mechanism of *closo*-$B_{10}H_{10}{}^{2-}$ [8, 9, 21–23]. Compound **1** is formed *via* a thioacetic acid-mediated cage-opening, a metal insertion and a desulfurization process. Few examples are known in the literature in which a thioacetic acid derivative is desulfurized to give the corresponding acetate product. In the $BF_3{\cdot}OEt_2$-mediated reaction of MeCOSH and methyl phenyldiazoacetate $[PhC(N_2)COOMe]$ the initially formed *O*-ester PhCH(OC(S)Me)COOMe was not stable and could be hydrolyzed during workup to give PhCH(OC(O)Me)COOMe [24]. In this connection it was also reported that *closo*-$B_{12}H_{12}{}^{2-}$ and CH_3COSH gave the normal substitution product $[B_{12}H_{11}(SC(O)CH_3)]^{2-}$ [25]. As already mentioned in the Introduction, the same reactions in the presence of RCOOH failed (the same being true with $NiCl_2(PPh_3)_2$) to afford tractable products, which means that the presence of a sulfur atom here is important to the formation of **1**. As the reaction was worked up in air, it is likely that the formation of **1** was effected by oxygen, but an alternative route may be more likely, *viz.* the hydrolysis of reaction intermediate(s) with *B*-thioacetoxy [B-OC(S)Me] moietie(s) mediated/catalyzed by Lewis acidic species (*e. g.* platinaborane intermediates) during the workup process. Moreover, the remarkable difference between the same reactions with thioacetic acid and with thiobenzoic acid may be attributed to the different influence of the phenyl and methyl groups, although this appears to make no difference in the analogous reactions with $NiCl_2(PPh_3)_2$. More experimental studies are needed to give an answer to this question.

Molecular and crystal structure of **1**

The molecular structure and selected bond parameters of **1** are presented in Fig. 2. Compound **1** has the same type of *nido*-PtB_{10} cluster as the *B*-alkoxy analogs [1 – 7], but with an acetoxy group at the B8 atom of the open PtB_4 face. The Pt center further coordinates to two *exo*-polyhedral PPh_3 ligands. The Pt7–B8 and Pt7–B11 bond lengths in **1** of 2.299(6) and 2.319(6) Å, respectively, are longer that those of 2.237(6) and 2.208(6) Å for Pt7–B2 and Pt7–B6, suggesting that the Pt–B bonds involved in the open PtB_4 face are slightly weaker than the other two Pt–B bonds. Despite the presence of different *B*-substituents, the Pt-B distances are found to be similar to those reported for the analogous clusters, *e. g.* 2.214(7)∼2.303(7) Å for $[(PPh_3)_2PtB_{10}H_{11}\text{-8-}(OCH_3)]$, 2.178(16)∼2.326(16) Å for $[(PPh_3)_2PtB_{10}H_{11}\text{-8-}(OCHMe_2)]$, 2.205(6)∼2.327(6) Å for $[(PPh_3)_2PtB_{10}H_{11}\text{-9-}(O\mathit{i}Pr)]$ [5], 2.223(6)∼2.330(6) Å for $[(PPh_3)_2PtB_{10}H_{10}\text{-8,10-}(OEt)_2]$, 2.215(10)∼2.340(11) Å for $[(PPh_3)_2PtB_{10}H_{10}\text{-8,10-}(O\mathit{i}Pr)_2]$ [6], and 2.234(8)–2.311(7) Å for $[(PPh_3)_2PtB_{10}H_{10}\text{-9,10-}(H_{0.7}Cl_{0.3})_2]$ [12].

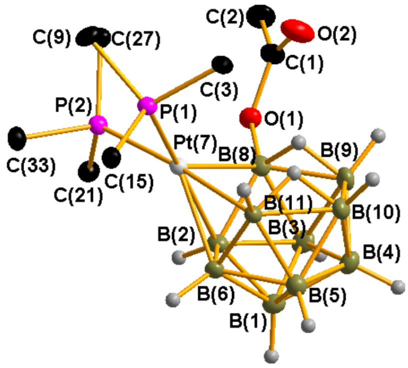

Fig. 2. The molecular structure of $[(PPh_3)_2PtB_{10}H_{11}\text{-11-}(OOCMe)]\cdot CH_2Cl_2$ (**1**), with atom labeling (25 % probability ellipsoids for non-H atoms). The dichloromethane solvent and the hydrogen atoms except those on the cluster have been omitted for clarity. For the same reason only the *ipso*-carbon atoms of the PPh_3 groups are shown. Selected bond lengths (Å) and angles (deg): Pt7–P1 2.3865(14), Pt7–P2 2.3689(13), Pt7–B8 2.299(6), Pt7–B11 2.319(6), Pt7–B2 2.237(6), Pt7–B6 2.208(6), B8–B9 1.860(9), B9–B10 1.938(10), B10–B11 1.859(8), B4–B9 1.742(10), B4–B10 1.735(10), B8–O1 1.424(7), O1–C1 1.358(7), C1–O2 1.190(7); P1–Pt7–P2 99.59(5).

In **1** the C1–O1 bond length is between those of a double bond (1.22 Å) and a single bond (1.43 Å), whereas the C(1)–O(2) bond shows a double bond character. The electron delocalization in the acetoxy moiety makes the B(8)–O(1) distance longer than those reported (1.35 – 1.39 Å) for the *B*-alkoxy-substituted structures mentioned above, but somewhat shorter than those found in the *B*-acyl-substituted boranes $[(RCOO)B_{12}H_{11}]^{2-}$ (R = Ph, Me, 1.494(12) and 1.485(3) Å, respectively) [26].

Interestingly, intramolecular C–H···O hydrogen bonds in the structure of **1** (Fig. 3) are found with the H4A···O2 distance of 2.51 Å (C4···O2 3.338(8) Å, C4–H4A···O(2) 149° and the H22···O1 distance of 2.58 Å (C22···O1 3.123(8) Å, C22–H22···O1 117°. In addition, intramolecular C–H···H–B dihydrogen bonding interactions are present involving the B6 atoms at the lower belt. The corresponding H16···H6 distance of 2.24 Å (C16···B6 3.662(8) Å, C16–H16···H6 angle 170.3°, H16···H6–B6 109.9° is shorter than the sum of the van der Waals radii of hydrogen atoms (2.4 Å) and well within the generally accepted values (1.8 – 2.3 Å) for such dihydrogen bonds [27, 28]. The molecules are further linked by intermolecular C–H···O hydrogen bonds (H25···O2 2.52 Å, C25···O2 3.356(8) Å and C25–H25···O2 150°) into a supramolecular chain structure, as demonstrated in Fig. 3.

The isolation and characterization of the unexpected product **1** provides an interesting aspect regarding the cage opening mechanism of $B_{10}H_{10}{}^{2-}$ with thiocarboxylic acids in the presence of a transition metal complex. In addition, the existence of multiple hydrogen bonding interactions in the structure of **1** shows the

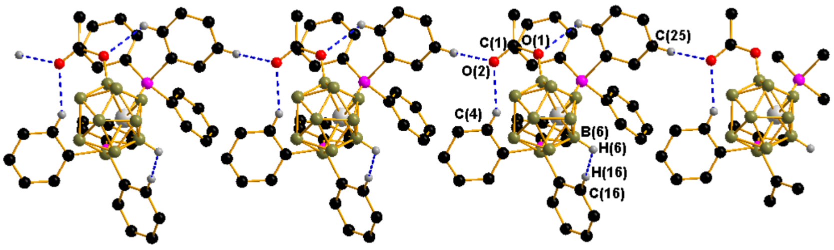

Fig. 3. The chain formed by intermolecular C–H···O hydrogen bonding in **1**. The intramolecular C–H···H–B dihydrogen bonds and C–H···O hydrogen bonds are also shown.

potential of metallaborane clusters for the construction of supramolecular assemblies, which is currently under study in our group.

Experimental Section

General

The synthesis was carried out under a dry nitrogen atmosphere, while the subsequent workup was performed in air. Solvents (dichloromethane, petroleum ether and *n*-hexane, analytically pure) were commercially available. The solvent used for reaction (dichloromethane) was dried, distilled, and saturated with nitrogen prior to use. Preparative thin-layer chromatography (TLC) was performed on glass plates (20 × 20 cm^2) with silica gel GF-254. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer (^{1}H: 399.89 MHz, ^{11}B: 128.30 MHz) in $CDCl_3$. $BF_3 \cdot OEt_2$ was used as the external standard for ^{11}B NMR. As internal reference for ^{1}H NMR, the signal of $CDCl_3$ was used, and the shifts were calculated relative to TMS. MS: ZAB-2F VH Micromass CTD and JEOL MS Station JMS 700 spectrometers. The starting materials $[Et_4N]_2B_{10}H_{10}$ [29] and $PtCl_2(PPh_3)_2$ [30] were prepared according to the literature.

*Synthesis of the platinaborane **1***

$PtCl_2(PPh_3)_2$ (314 mg, 0.4 mmol), $(Et_4N)_2B_{10}H_{10}$ (150 mg, 0.4 mmol), CH_3COSH (0.07 mL, 0.98 mmol), and CH_2Cl_2 (40 mL) were put into a 100-mL Schlenk flask, and the mixture was refluxed for 34 h. The resulting orange solution was concentrated to *ca*. 5 mL and chromatographed using dichloromethane-petroleum ether (4 : 1, v/v) as the eluting medium. An orange band (R_f = 0.6) was separated and further purified by TLC [dichloromethane/petroleum ether (4 : 1, v/v)] to give a yellow band (R_f = 0.5), from which a yellow solid (53 mg, 13.5 %, based on $B_{10}H_{10}{}^{2-}$) was obtained. Yellow crystals suitable for X-ray diffraction were grown by the diffusion method [dichloromethane/*n*-hexane(1 : 4, v/v)] after 24 h at r. t. – Anal. for $C_{39}H_{46}B_{10}Cl_2O_2P_2Pt$: calcd. C 47.66, H 4.72; found C 47.75, H 4.71 %. – IR (KBr): ν = 3437 (s), 2924 (w), 2541 (s), 1732 (s), 1435 (s), 1096 (s), 694 (s) cm^{-1}. – ^{1}H NMR: $\delta = -2.55$ (s, br. 2H, BHB), 1.411 (s, 3H, Me), 7.26 – 7.80 (m, 30H, PhH) ppm. – ^{11}B NMR: $\delta = -29.8, -21.7, -11.9, -5.8$, 3.9, 13.1, 21.2, 24.7 ppm. – MS ((+)-FAB): m/z (%) = 983 (100) $[M+CH_2Cl_2]^+$, 898 (62) $[M]^+$. – HRMS ((+)-FAB): m/z = 899.3388 (calcd. 899.3394 for $C_{38}H_{44}O_2P_2^{11}B_{10}^{195}Pt$, $[M]^+$; $\Delta m = -0.7$ mmu).

*X-Ray diffraction study of the platinaborane **1** · CH_2Cl_2*

$C_{39}H_{46}B_{10}Cl_2O_2P_2Pt$, M_r = 982.79, monoclinic, space group $P2_1/c$, a = 10.3542(18), b = 17.977(2), c = 23.498(3) Å, β = 91.668(2)°, V = 4372.1(11) Å^3, T = 298(2) K, Z = 4, $\mu(MoK_\alpha)$ = 3.4 mm^{-1}, crystal size $0.53 \times 0.47 \times 0.39$ mm^3. The intensity data were collected on a Bruker Smart-1000 CCD diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were corrected for Lorentz polarization and absorption effects (semi-empirical, SADABS [31]). The structure was solved by Direct Methods (SHELXS-97) [32] and refined by least-squares methods based on F^2 with all measured reflections (SHELXTL) [33]. The bridging hydrogen atoms were located in the difference Fourier map, and other hydrogen atoms were placed at idealized geometrical positions. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Due to the disordered dichloromethane molecule 66 least-squares restraints were used in the refinement. The final refinement converged to $R_1 = 0.0337$ [for 7688 observed reflections with $I \geq 2\sigma(I)$] and $wR2$ = 0.0765 (for all unique reflections), GoF = 1.029; the number of refined parameters is 553.

CCDC 684601 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors thank the University of Jinan (No. B0605) and, in part, the NSFC (20702020) and SRF for ROCS, SEM (SQT0804) for financial support of this work.

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