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Reaction of a ruthenium B-carboranyl hydride complex and $BH_3(SMe_2)$: Selective formation of a pincer-supported metallaborane $LRu(B_3H_8)$

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ABSTRACT

Reaction of a boryl hydride pincer complex (POBOP)Ru(H)(PPh_3) (POBOP = 1,7-OP(*i*-Pr)$_2$-*m*-2-carboranyl) and $BH_3(SMe_2)$ at 70 °C led to the selective formation of a pincer-supported metallaborane (POBOP) Ru(B_3H_8). Single crystal structure of (POBOP)Ru(B_3H_8) was determined. This complex features coordination of the carborane cluster through adjacent boryl and borane groups that impose significantly different *trans*-influence on the coordinated B_3H_8 fragment.

1. Introduction

Boron clusters continue to attract attention due to their potential for application in inorganic chemistry, catalysis, polymers, batteries, medicine, luminescent materials, and liquid crystals [1–7]. Metallaboranes are related to both polyhedral boron clusters and multinuclear metal clusters as they often feature both multicentered metal-boron and metal-metal bonds [8–11]. One of the convenient methods of metallaborane synthesis is the reaction of transition metal halides or hydrides and monoborane sources (BH_3(THF) or $LiBH_4$) that led to the discoveries of a wide range of clusters from smallest trinuclear to large 20-vertex systems [12–16].

We have recently reported the synthesis of the first example of the (BB)-carboryne complex (POBBOP)Ru(CO)$_2$ (**1**) which features a strained (BB)>Ru three-membered metallacycle (POBBOP = 1,7-OP(*i*-Pr)$_2$-2,6-dehydro-*m*-carborane) [17]. We have shown that boryl centers of (BB)-carboryne are strongly nucleophilic and react with variety of electrophiles. Instead of producing a metallaborane, the reaction of the carboryne complex and $BH_3(SMe_2)$ led to the formation of the exohedral B—B bond between the boron cluster and the borylhydroborate group (Scheme 1). This transformation was the first example of the regioselective formation of an exohedral B—B bond between a carborane and a borane under metal-promoted conditions.

Subsequently, we have reported the synthesis of the pincer complex (POBOP)Ru(H)(PPh_3) (**2**), which featured a boryl, borane, and hydride ligands at the ruthenium center (POBOP = 1,7-OP(*i*-Pr)$_2$-*m*-2-carboranyl) [18]. The presence of the bridging B—H···Ru interaction vicinal to the B—Ru bond led to the significant distortion of the metal-boryl bond that manifested in an acute exohedral angle of 69.4(2)° between this bond and the cluster (for comparison, an unstrained exohedral angle for an idealized icosahedron is 120°).

In this work, we explored the reaction of **2** and $BH_3(SMe_2)$ to probe whether the strained nucleophilic metal-boron bond will be a reaction center analogous to that in the (BB)-carboryne complex **1**, or if the terminal metal hydride group will interact with an incoming borane to form a metallaborane. We found that the latter outcome is in operation as this reaction exclusively produced (POBOP)Ru(B_3H_8) complex (Scheme 1).

2. Results and discussion

The reaction of (POBOP)Ru(H)(PPh_3) and excess BH_3(THF) at 70 °C in THF for 16 h led to the clean formation of a single product

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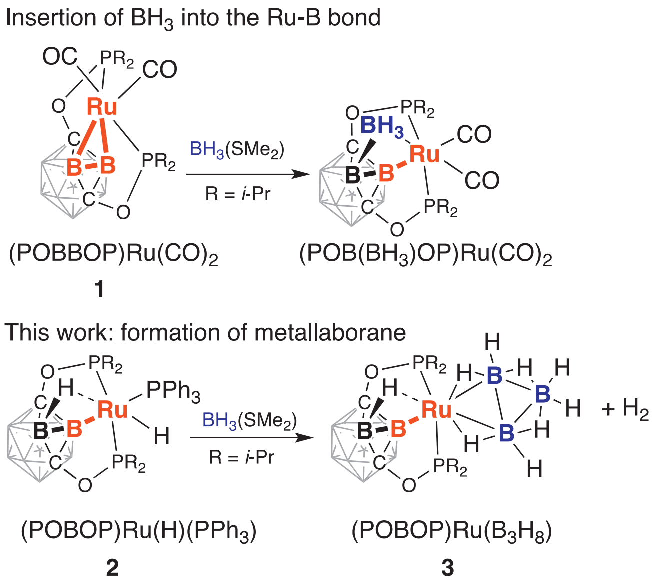

Scheme 1. Reactions of (BB)-carboryne complex (POBBOP)Ru(CO)$_2$ (**1**) and carboranyl hydride complex (POBOP)Ru(H)(PPh$_3$) (**2**) with BH$_3$(SMe$_2$).

according to ^{31}P NMR spectroscopy. In the spectrum of the reaction mixture, a set of two doublets was observed indicating inequivalence of two phosphinite arms in the product. The product was isolated as light brown solid in 69% yield.

Single crystals were grown from an acetonitrile solution by slow solvent evaporation at room temperature. The single crystal X-ray diffraction study revealed the molecular structure of (POBOP)Ru(B$_3$H$_8$) (**3**, Fig. 1). The asymmetric unit consists of half of one complex, which is located on a crystallographic mirror plane. The B$_3$H$_8$ fragment bonded to the ruthenium atom is disordered across the mirror plane. The structure can be described as the seven skeletal electron pair *arachno* LRuB$_3$H$_8$ cluster derived from the butterfly-shaped cluster B$_4$H$_{10}$, in which one of the BH$_2$ groups is replaced by the ruthenium center. The carborane cluster is coordinated to the metal center through the 2c-2e Ru—B bond (2.143(2) Å) and the 3c-2e B—H···Ru bridging interaction (B2(H2)···Ru1 distance is 2.265(2) Å). This bridging interaction features the shortest Ru···B distance for a neutral carborane cluster reported to date. The closeness of the metal-boron distances for these two distinctly different coordination interactions results in the severe strain of the metal-boryl B1—Ru1 bond. An unstrained bond angle for an exohedral substituent on the idealized icosahedral cluster is 120° while the B2—B1—Ru1 angle in **2** is acute at 70.7(1)°. This dramatic distortion of the exohedral bonding is due to the propensity of the metal center to strongly coordinate to the vicinal B—H bond in addition to coordination to the carborane cluster through the metal-boryl bond within the POBOP pincer framework.

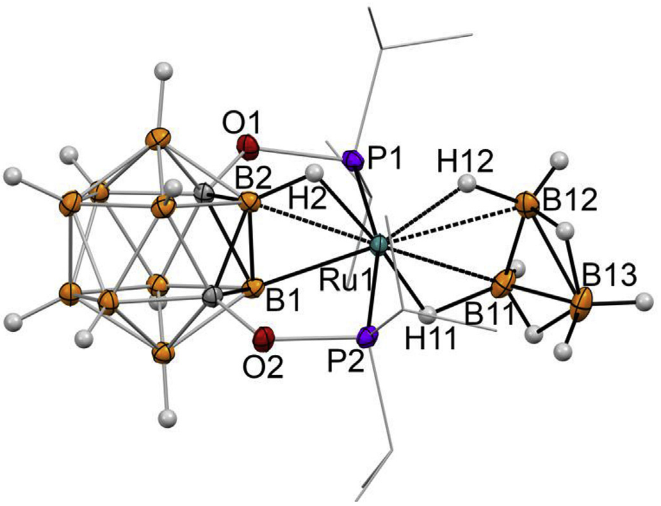

Fig. 1. Displacement ellipsoid plot (50% probability) of (POBOP)Ru(B$_3$H$_8$) (POBOP = 1,7-OP(*i*-Pr)$_2$-2-dehydro-*m*-carboranyl) (**3**). Atoms belonging to isopropyl groups of the ligand arms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1—B1 = 2.143(2), Ru1···B2 = 2.265(2) Å, Ru1···B11 = 2.361(4), Ru1···B12 = 2.441(3), B11—B12 = 1.747(5), B11—B13 = 1.787(5), B12—B13 = 1.798(5), B2—B1—Ru1 = 70.7(1).

The B$_3$H$_8$ anion is coordinated to the ruthenium center through two B—H···Ru bridging interactions. The B12 atom is *trans*-to the anionic boryl center B1 and the B11 atom is *trans*-to the neutral borane center B2(H2). The strong *trans*-influence of the boryl anion results in the significantly longer B12(H)···Ru1 distance (2.441(3) Å) than the B11(H)···Ru1 distance (2.361(4) Å). The B—B bond lengths in the B$_3$H$_8$ fragment in **2** are comparable with those in complexes with the related geometry [19,20].

The dihedral angle between the planes Ru1—B11—B12 and B11—B12—B13 is 122.6°, which is within the typical range for *arachno*-2-metallatetraboranes. The B$_3$H$_8$ fragment is tilted relative to the mirror plane of the carborane cluster with the dihedral angle between planes B2—B1—Ru1 and Ru1—B11—B12 of 11°.

The NMR spectra of **2** in solution are consistent with its molecular structure. The presence of two sharp doublets in the ^{31}P NMR spectrum indicates the static coordination of the B$_3$H$_8$ fragment to the metal center. As the B$_3$H$_8$ anion is bent, it causes inequivalence between phosphinite groups of the pincer ligand. The ^{1}H NMR spectrum features a signal from the bridging carborane-metal interaction B—H···Ru at −9.62 ppm as a 1:1:1:1 quartet with $J_{BH} = 100$ Hz (Fig. 2). In addition, signals from the B$_3$H$_8$ group are observed with two protons of the B—H···Ru bonds at −5.48 and −13.37 ppm and two B—H—B protons at −0.38 ppm. The remaining three signals from terminal BH and BH$_2$ protons overlap with signals from BH groups of the carborane cluster. The ^{11}B NMR spectrum contains partially overlapping signals from the boron cluster at −11 to −19 ppm, a signal from the metalated boron vertex at −3.0 ppm and three signals from the B$_3$H$_8$ fragment at 3.16, −36.2, and −42.3 ppm.

The coordination sphere of the ruthenium center is a distorted octahedron with one boryl ligand, one borane group of the cluster and two borane groups of the B$_3$H$_8^-$ anion. The chemical shift difference between the boron atoms of the B$_3$H$_8^-$ anion is indicative of a strong *trans*-influence of the boryl part of the POBOP ligand.

Formation of metallaboranes containing B$_3$H$_8^-$ fragment has been observed in reactions of cyclopentadienyl complexes of Fe(I), Mo(I), Re(VII), or W(PMe$_3$)H$_6$ with BH$_3$(THF) [12,16,19]. Notably, thermolysis of Cp*Ru(PMe$_3$)(B$_2$H$_7$) led to the formation of Cp*Ru(PMe$_3$)(B$_3$H$_8$) in trace quantities [20]. In our case, the presence of the terminal hydride functionality appears to drive the reaction towards the selective formation of the Ru(B$_3$H$_8$)$^+$ moiety. It has been shown that the *arachno*-2-metallaboranes L$_n$MB$_3$H$_8$ can convert upon thermolysis into *arachno*-1 complexes through wing-to-hinge isomerization [19,20]. Heating **3** at 110 °C in toluene for 24 h did not lead to any changes in ^{31}P NMR spectra of the sample, indicating that no thermal rearrangement occurred. Furthermore, the metallaborane **3** was found to be stable towards reactions with electrophiles such as CH$_3$I and PhCH$_2$Br.

3. Summary

The reaction of (POBOP)Ru(H)(PPh$_3$) that possesses both

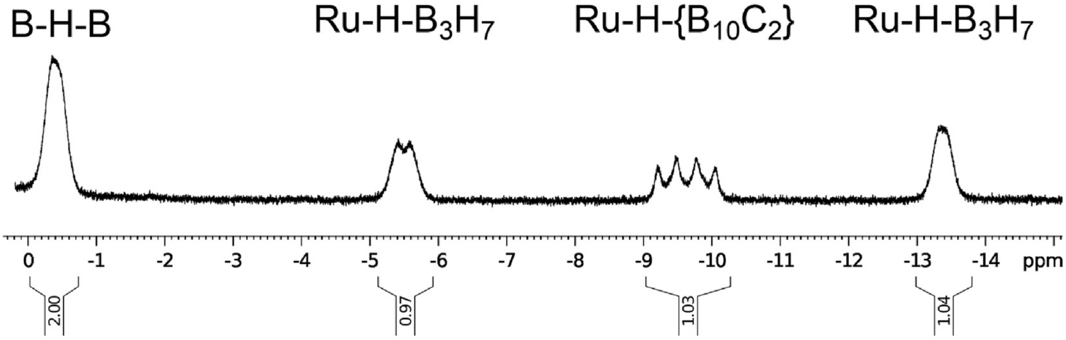

Fig. 2. A portion of the ^1H NMR spectrum of (POBOP)Ru(B_3H_8) (**3**) in C_6D_6 featuring signals from Ru···(H)(B) bridging protons.

nucleophilic boryl and terminal metal hydride reaction sites with $BH_3(SMe_2)$ led to the selective formation of the *arachno*-2-metallaborane (POBOP)Ru(B_3H_8) through the interaction of the borane with the Ru—H bond. (POBOP)Ru(B_3H_8) features coordination of the carborane cluster through adjacent boryl and borane groups.

4. Experimental

All synthetic manipulations were carried out either in a nitrogen-filled drybox or on an air-free dual-manifold Schlenk line, unless stated otherwise [21]. The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Benzene-d_6 was degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 (^1H), 100 (^{13}C), 162 (^{31}P), 128 (^{11}B) MHz, reported in δ (parts per million) and referenced to the residual $^1H/^{13}C$ signals of the deuterated solvent or an external 85% H_3PO_4 (^{31}P (δ): 0.0 ppm) and $BF_3(Et_2O)$ ($^{11}B(\delta)$: 0.0 ppm) standards. J values are given in Hz. Midwest Microlab, Indianapolis, Indiana provided the elemental analysis results.

POBOP(Ru)(H)(PPh_3) (POBOP = 1,7-OP(i-Pr)$_2$-m-2-carboranyl) (**2**) was prepared using the previously reported procedure [18]. $Ru(PPh_3)_3Cl_2$ (Strem), m-carborane $C_2B_{10}H_{12}$ (Katchem), and $BH_3(SMe_2)$ (1 M solution in THF) were used as received.

4.1. Synthesis of (POBOP)Ru(B_3H_8) (3)

A portion of (POBOP)Ru(H)(PPh_3) (0.025 g; 0.032 mmol) was dissolved in 1.5 mL of benzene and then transferred to a J. Young valve NMR tube. A portion (0.17 mL, 0.17 mmol; 5.3 equiv.) of a 1 M solution of $BH_3(SMe_2)$ in THF was then added and the reaction mixture was heated at 70 °C for 16 h. The resulting dark brown solution was then dried under vacuum, triturated with acetonitrile (3 × 1 mL), filtered, and triturated with hexanes (3 × 1 mL) to yield light brown powder. Yield: 0.012 g, 0.022 mmol, 69%.

^{1}H (C_6D_6): δ 4.8–0.5 (br. 10H, $C_2B_{10}H_{10}$), 1.87 (m, 1H, $CH(CH_3)_2$), 1.68 (m, 3H, $CH(CH_3)_2$), 1.25 (m, 6H, $CH(CH_3)_2$), 0.97 (m, 6H, $CH(CH_3)_2$), 0.86 (m, 6H, $CH(CH_3)_2$), 0.71 (m, 6H, $CH(CH_3)_2$), −0.38 (br, 2H, B-*H*-B), −5.59 (br, 1H, Ru-*H*-B), −9.62 (q, JBH = 100 Hz, 1H, Ru-*H*-B), −13.37 (br, 1H, Ru-H-B). **^{11}B{^{1}H}** (C_6D_6): δ 3.16, −2.98, −10.95, −13.26, −13.57, −16.05, −17.07, −19.03, −36.15,- −42.32. **^{13}C** (C_6D_6): δ 30.3 ($CH(CH_3)_2$), 29.6 ($CH(CH_3)_2$), 27.5 ($CH(CH_3)_2$), 19.4 ($CH(CH_3)_2$), 18.7 ($CH(CH_3)_2$), 18.2 ($CH(CH_3)_2$), 17.8 ($CH(CH_3)_2$), 16.9 ($CH(CH_3)_2$), 14.8 ($CH(CH_3)_2$). A signal from carbon atoms of the carborane cluster was not observed.

^{31}P{^{1}H} (C_6D_6): δ 217.1 (d, 1P), 211.0 (d, 1P). Cald. for $C_{14}H_{45}B_{13}O_2P_2Ru$: C, 30.62; H, 8.26. Found: C, 30.98; H, 7.84.

4.2. Crystal data

For POBOP(Ru)(B_3H_8) (**2**) (M = 549.04 g/mol): orthorhombic, space group *Pnma* (no. 62), a = 9.5885(5) Å, b = 18.2114(9) Å, c = 15.5618(7) Å, V = 2717.4(2) Å^3, Z = 4, T = 100(2) K, $\mu(MoK_\alpha) = 0.707\ mm^{-1}$, $D_{calc} = 1.342\ g/cm^3$, 44433 reflections measured ($4.474° \le 2\Theta \le 60.112°$), 4096 unique ($R_{int} = 0.0536$, $R_\sigma = 0.0278$) which were used in all calculations. The final R_1 was 0.0257 ($I > 2\sigma(I)$) and wR_2 was 0.0573 (all data).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 1885710. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223−336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.02.010.

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