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Special Collection

Bis(pentafluorophenyl)borane Induced Tandem Hydroboration-Carboboration of Cyclooctatetraene

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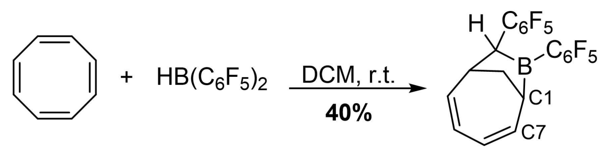
We report here the formation of the bridged boracycle **1** upon reaction of cyclooctatetraene with bis(pentafluorophenyl)borane. Computations indicate that the reaction commences with a hydroboration and that the high Lewis acidity of the bis(pentafluorophenyl)borane then induces a rearrangement with cleavage of a carbon–carbon bond via a nonclassical zwitterion and a final 1,1-carboboration. An intermediate of the reaction was captured as tri-*tert*-butylphosphine adduct.

The hydroboration of olefins and alkynes is a ubiquitous operation in organic synthesis. Although direct carboboration of unsaturated organic molecules forms a C–C bond and simultaneously incorporates a boryl unit in an organic framework, this type of reaction is less frequently employed. However, in the last decade, there have been a number of reports of direct carboborations with Lewis acidic boranes. A prime example is the 1,1-carboboration of alkynes by tris(pentafluoro)phenylborane (BCF) that was reported independently by the groups of Erker and Berke.[1] Meanwhile, a variety of alkynes, alkenes, and olefins have been shown to readily undergo 1,1-carboborations with BCF.[2] Furthermore, 1,2-carboborations of alkynes and allenes by pentafluorophenyl boranes have been reported.[3] The 1,2-carboboration of alkynes was also achieved with borenium ions and Lewis acidic haloboranes.[4] In 2017, Woerpel and co-workers reported the carboboration of a highly strained *trans*-alkene, embedded in a seven-membered silyl ether, by triethylborane.[5] One year later, Studer reported the photochemical 1,2-carboboration of olefins using bis(catecholate)diboron as boron source in combination with an alkylhalide.[6] This reaction proceeds via a radical pathway. We now found that the reaction of bis(pentafluorophenyl)borane ($HB(C_6F_5)_2$) with cyclooctatetraene (COT) leads to the formation of bridged boracycle **1** that was isolated by crystallization in 38% yield (Scheme 1). During the reaction, the $HB(C_6F_5)_2$ transferred a hydrogen and a pentafluorophenyl-substituent to the COT. Thus, this reaction is an example of tandem hydroboration-carboboration of a non-cumulated π-system. Furthermore, ring contraction and rearrangement with cleavage of a carbon-carbon bond occurred in the course of the reaction.

Crystals of **1**, suitable for single-crystal X-ray diffraction (SCXRD), were grown from a concentrated *n*-hexane solution at −35 °C (Figure 1). SCXRD analysis supports the structural assign-



Scheme 1. Formation of **1** upon reaction of COT with $HB(C_6F_5)_2$ (DCM = dichloromethane).

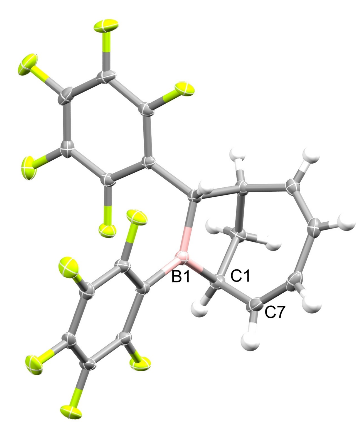


Figure 1. Molecular structure of **1** derived from SCXRD (50% probability ellipsoids). Selected bond lenghts and angles: C1–B1: 1.577(2) Å, C1–C7: 1.509(2) Å, B1–C1–C7: 92.26°.

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ment and reveals a short distance between the boron center and carbon C7 (2.225 Å). Furthermore, the B–C1–C7 angle (92.26 °) deviates significantly from the ideal angle at a tetrahedral carbon. We computationally optimized the structure of **1** with the PBEh-3c method, which has been shown to yield reliable structures.[7] The computed structural features agree well with those derived from SCXRD, which indicates that the short B–C7 distance and the B–C1–C7 angle are not due to packing effects. This indicates that attractive interactions between the Lewis acidic borane and the π-electron density at C7 are responsible for the short B–C7 distance and the narrow angle at C1.[8] To further substantiate this assumption, we computed the structure of a derivative of **1** with a methoxy substituent in place of the pentafluorophenyl substituent on boron. This derivate indeed shows lengthening of the B–C7 distance to 2.48 Å as well as a substantial widening of the B–C1–C7 angle to 106.3°. We then focused on elucidating the mechanism that leads to the formation of **1**. Different pathways were considered computationally at the revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c level of theory with the PCM solvation model for dichloromethane.[7,9] For brevity, only the kinetically preferred pathway is discussed here (Figure 2); alternative pathways can be found in the Supporting Information.

The pathway commences with the hydroboration of COT, which yields the borylsubstituted cyclooctatriene **2**. Addition of the borane to the π-bond at the opposite side of the ring leads to the formation of the zwitterion **3**, in which the positive charge is resonance stabilized. The formation of **3** is endergonic but fast with a barrier of 6.9 kcal mol^{-1}. Unexpectedly, we found a kinetically accessible transition state **TS$_{3/4}$** that converts **3** to the zwitterion **4**. According to the Lewis notation, the positive charge in **4** is located at a secondary carbon. However, a closer look at the computed structure showed that the distance between this carbon and the bridgehead carbon is only 1.62 Å, indicating a bonding interaction. Further computations at PBE0/def2-TZVPP indeed revealed a negative value of the Laplacian of the electron density at the bond critical point between these two carbon centres (see Supporting Information, Figure SI 32). Thus, the bridgehead carbon is pentavalent and **4** can be described as nonclassical zwitterion. However, **4** is a high-lying

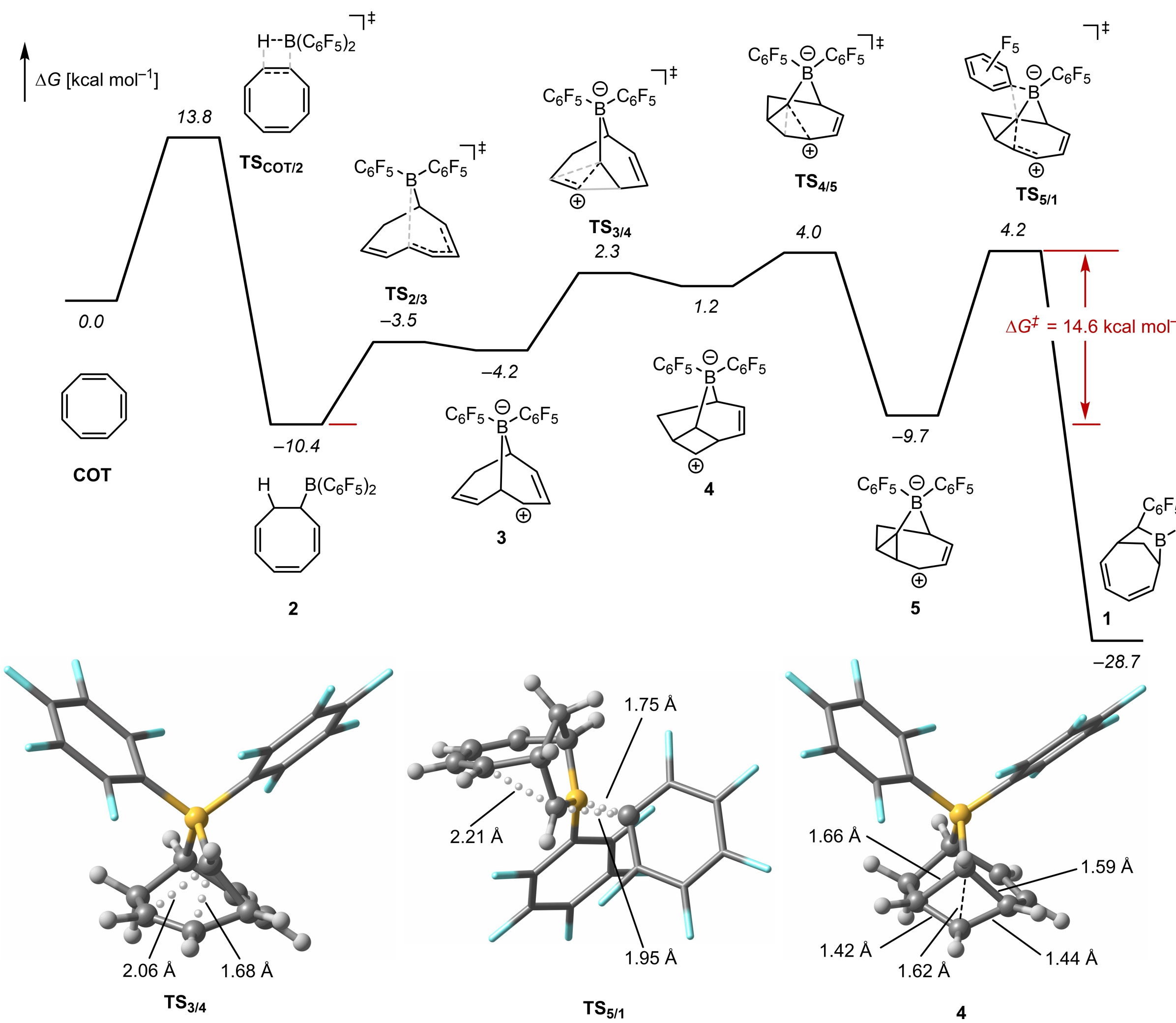
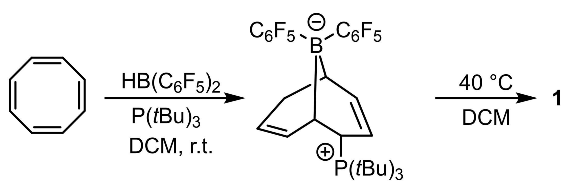


Figure 2. PES for the formation of **1** at PCM(DCM)-revDSD-PBEP86-D4/def2-QZVPP//PCM(DCM)-PBEh-3c. The Insets show the computed structures of **TS$_{3/4}$** yielding the "non-classical" zwitterion **4**, the minimum structure of **4** and the product forming **TS$_{5/1}$**.

intermediate that rearranges via a low barrier of 2.8 kcal mol^{-1} to more stable zwitterion **5**. This step represents a ring-contraction. Ring-opening of the cyclopropyl ring in **5** induces the transfer of a pentafluorophenyl-substituent from boron to the adjacent carbon. To provide experimental support for the mechanistic proposal, we attempted to capture intermediates of the transformation that leads to **1**. We envisioned that a Lewis base might allow us to capture one of the zwitterionic intermediates that are computed to be part of the reaction. To avoid quenching the Lewis acidity of $HB(C_6F_5)_2$, we decided to use a sterically encumbered Lewis base. This approach can be viewed as an attempt to trap an intermediate by a frustrated Lewis pair (FLP) formed in situ. Upon addition of COT to an equimolar mixture of $HB(C_6F_5)_2$ and tri-*tert*-butylphosphine (P(*t*Bu)$_3$) in DCM, the formation of a new species was observed with a ^{31}P NMR shift of 59.8 ppm, indicating a phosphine adduct (Scheme 2). This new species was isolated in 43% yield by crystallization from DCM/*n*-hexane. The SCXRD structure showed that the P(*t*Bu)$_3$ adduct of intermediate **3** was obtained (Figure 3).

We note that the structure of **3-P(*t*Bu)$_3$** is indeed reminiscent of an olefin captured by an FLP.[10] When a DCM-d_2 solution of **3-P(*t*Bu)$_3$** is heated to 40 °C, the formation of **1** and free P(*t*Bu)$_3$ is observed. Thus, this experiment supports that **3** is indeed part of the reaction path that leads to the formation of **1**, which in turn supports the assumption that the nonclassical zwitterion **4** formed from a rearrangement of **3** is a plausible intermediate. Further evidence that the calculated mechanism is indeed the productive mechanism is provided by deuterium labeling experiments. When COT is reacted with bis(pentafluorophenyl)borane-d_1 ($DB(C_6F_5)_2$) under the same



Scheme 2. Formation of **3-P(*t*Bu)$_3$** upon reaction of COT with P(*t*Bu)$_3$ and $HB(C_6F_5)_2$.

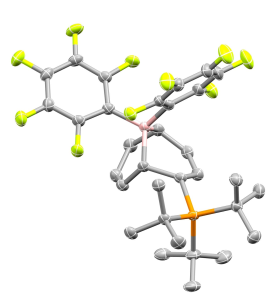
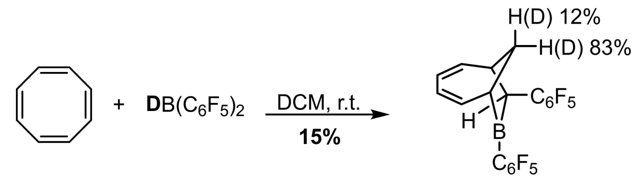


Figure 3. Molecular structure of **3-P(*t*Bu)$_3$** derived from SCXRD (50% probability ellipsoids, all hydrogens and a second independent molecule are omitted for clarity).



Scheme 3. Formation of **1-*d*$_1$** upon reaction of COT with $DB(C_6F_5)_2$. The percentage of deuterium incorporation is given.

reaction conditions as described above, the highest deuterium incorporation is found at the methylene bridge of the product (Scheme 3). In the ^{1}H NMR spectra of **1**-d_1, the proton signal of hydrogen at the *exo*-position of the methylene bridge is decreased by 60%. The corresponding *endo*-^{1}H signal is also decreased by 20%. The ^{2}D NMR of **1**-d_1 shows only these two positions with significant D incorporation (83% and 12% by integration of the ^{2}D NMR).

According to the computed mechanism, deuterium incorporation in the *exo*-position is expected. In summary, we have documented that the hydroboration of COT by bis(pentafluorophenyl)borane initiates a rearrangement of the carbon skeleton and a 1,1-carboboration. The findings reported herein might stimulate the development of synthetic methods that rely on Lewis acid-induced rearrangements.

Experimental Section

All manipulations were carried out in a nitrogen filled glove box (mBraun Uni Lab plus) or using standard Schlenk techniques. Dry and non-deuterated Solvents were purchased from ACROS organics and used as is. Acetonitrile was filtered through a 0.22 µm PTFE syringe-filter prior to use. Deuterated solvents were degassed with at least three freeze-pump-thaw cycles and stored for at least 24 h over molecular sieves inside the glovebox prior to use. Commercially available COT was distilled under an inert atmosphere and stored in the Glove box at −35 °C. $HB(C_6F_5)_2$ was synthesised from BCF by literature known procedures.[11] $DB(C_6F_5)_2$ was synthesized analogously from BCF and $PhMe_2Si$–D, which was prepared by a modified literature procedure.[12] See SI for detailed procedures and NMR-Spectra.

Synthesis of 1: COT (33.4 µL, 31.2 mg, 0.3 mmol, 1.0 equiv.) was dissolved in 1 mL DCM and a stirring bar was added. $HB(C_6F_5)_2$ (104 mg, 0.3 mmol, 1.0 equiv.) was dissolved in 3 mL DCM and added dropwise to the COT-solution. After the addition, the vial was closed and stirred overnight (18 h) at room temperature. The solvent was then removed under vacuum. The residue was taken up in a minimal amount of *n*-hexane (approx. 4 mL) and the resulting solution was filtered through a 0.22 µm PTFE filter. After standing at −35 °C, **1** crystalized in white to beige needles. After removal of the supernatant, washing with small portions of cold *n*-hexane and evaporation of the solvent to dryness 41 mg (30%) of **1** were isolated. Upon drying of the supernatant and crystallization from cold *n*-hexane a second fraction of 11 mg (8%) of **1** could be isolated. The crystals obtained in the first crystallization were also suitable for SC-XRD. ^{1}H NMR (600 MHz, chloroform-*d*) = δ 6.50 (dd, J = 9.1, 10.7 Hz, 1H, H-C_{sp2}), 6.20 (dd, J = 11.4, 7.3 Hz, 1H, H-C_{sp2}), 6.00 (dd, J = 10.8, 7.3 Hz, 1H, H-C_{sp2}), 5.58 (dd, J = 9.0, 11.2 Hz, 1H, H-C_{sp2}), 3.96 (t, J = 6.4 Hz, 1H, $C_{sp3}H$), 3.18 (s, 1H, H_{bn}), 2.73 (t, J = 8.0 Hz, 1H, $C_{sp3}H$), 2.42 (dt, J = 12.3, 6.0 Hz, 1H, CH_2), 1.62 (d, J = 12.7 Hz, 1H, CH_2). $^{13}C\{^1H,^{19}F\}$ NMR (101 MHz, chloroform-d) = δ 151.10–150.00 (m, C_{Ar}), 144.79 (s, C_{Ar}), 144.17 (s, C_{Ar}), 140.93 (s, $C_{olefinic}$), 139.57 (s, C_{Ar}), 137.72 (s, C_{Ar}), 137.56 (s, C_{Ar}), 130.87 (s, $C_{olefinic}$), 124.03 (s, $C_{olefinic}$), 121.87 (s, $C_{olefinic}$), 118.04 (s, $C_{Ar,q}$), 107.84 (s, B-$C_{Ar,q}$), 48.81 (br, B-C_{sp3}), 47.58 (s, C_{sp3}), 40.18 (br, C_{bn}), 29.83 (CH_2). ^{11}B NMR (193 MHz, chloroform-d) = δ 52.2. ^{19}F NMR (377 MHz, benzene-d_6) = δ −126.03 (dq, J = 20.7, 7.2, 6.0 Hz, 2F), −137.64 (br, 2F), −146.55 (tt, J = 20.3, 6.2 Hz, 1F), −157.55 (t, J = 20.9 Hz, 1F), −161.22 (tt, J = 20.4, 6.3 Hz, 2F), −161.82 (td, J = 22.4, 7.0 Hz, 2F). Elemental analysis calc (%) for $C_{20}H_9BF_{10}$: C 53.37, H 2.02, N 0, found: C 53.27, H 2.02, N 0.14.

Synthesis of 3-P(*t*Bu)$_3$: $HB(C_6F_5)_2$ (64.7 mg, 0.184 mmol; 1.0 equiv.) and $P(tBu)_3$ (39.8 mg, 0.193 mmol; 1.05 equiv.) were dissolved in 4 mL DCM in a 20 mL Schlenk-finger with J-Young Valve. While stirring the solution, COT (20.7 μL, 19.1 mg; 1.0 equiv.) was added via an Eppendorf pipette. After the addition, the neck of the J-Young tube was washed with 1 mL DCM and the Schlenk-finger closed off. After stirring for 2 h at r.t., the solvent was evaporated under vacuum. The resulting residue was dissolved in a minimal amount of DCM (appr. 1 mL) and filtered through a 0.22 μm PTFE filter. Crystallization of **3-P(*t*-Bu)$_3$** was archived by overlaying the DCM solution with *n*-hexane (appr. triple volume) and slow diffusion overnight or several days. After removal of the supernatant, the obtained crystals were washed with n-hexane and small volumes of DCM. After drying 51.9 mg (43 %) of **3-P(*t*-Bu)$_3$** could be obtained. ^1H NMR (400 MHz, CD_2Cl_2) = δ 6.26 (s, 1H, H-C_{sp2}), 5.97 (t, J = 8.4 Hz, 1H, H-C_{sp2}), 5.66–5.52 (m, 2H, H-C_{sp2}), 3.55 (d, J = 16.2 Hz, 1H, H-CP(tBu)$_3$), 2.98 (s, 1H, C_{sp3}), 2.42 (s, 1H, C_{sp3}), 1.84 (s, 2H; CH_2), 1.57 (d, J = 13.2 Hz, 27H, P(tBu)$_3$).^{13}C NMR (101 MHz, CD_2Cl_2) = δ 145.77 (d, J = 11.2 Hz, C_{sp2}), 133.41 (C_{sp2}), 130.78 (C_{sp2}), 118.39 (C_{sp2} (d, J = 15.0 Hz), 40.83 (d, J = 23.9 Hz, P(**C**(Me)$_3$)$_3$), 33.08 (d, J = 1.9 Hz, CH_2), 31.66 (P(C(CH_3)$_3$)$_3$). ^{31}P NMR: (126 MHz, CD_2Cl_2) = δ 59.8. ^{11}B NMR (128 MHz, CD_2Cl_2) = δ −11.78. ^{19}F NMR (377 MHz, CD2Cl2) - = δ −130.12 (dt, 1 F, J = 26.1, 9.7 Hz, F_{10}), −133.54 (dt, 2 F, J = 24.9, 9.4 Hz, $F_{5/6}$), −135.87 (dt, 1F, J = 25.6, 10.1 Hz, F_1), −162.67 (t, 1 F, J = 20.0 Hz, F_8), −164.55 (t, 1 F, J = 20.6 Hz, F_3), −165.00–−165.38 (m, 1 F, F_7), −166.13–−166.59 (m, 1 F, F_9), −167.28 (dp, 2 F, J = 31.9, 10.0 Hz, $F_{2/4}$).

HRMS (ESI) m/z [M + K +] calc. $C_{32}H_{36}BF_{10}P + K^+$: 691.213; found 691.212

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Hydroboration · Carboboration · Rearrangement · Density functional calculations · Lewis acid

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