Piers' Borane-Induced Tetramerization of Arylacetylenes

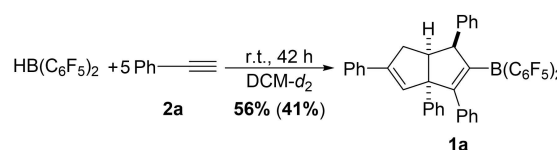Max Hasenbeck,[a] Tizian Müller,[a] Arthur Averdunk,[a] Jonathan Becker,[b] and Urs Gellrich*[a]

Abstract: We herein report that the reaction of Piers' borane, *i.e.* $HB(C_6F_5)_2$, with an excess of arylacetylenes at room temperature leads to tetramerization of the acetylene and the diastereoselective formation of boryl-substituted tetra-aryl-tetrahydropentalenes. The reaction mechanism was investigated by isotope labeling experiments and DFT computations. These investigations indicate that a series of 1,2-carboboration reactions form an octatetraene that undergoes an electrocyclization. Two skeletal rearrangements then presumably lead to the formation of the tetrahydropentalene core. Overall, this intricate and unprecedented transformation comprises five carbon-carbon bond formations in a single reaction.

Building molecular complexity from simple starting materials is paramount for synthetic chemistry. Boranes are in this context usually considered as reagents for transition metal-catalyzed C–C and C-Het couplings.[1,2] However, transformations of organic molecules, including skeletal rearrangements and C–C bond formations induced by highly Lewis acidic boranes have been reported recently. Prime examples are the 1,1-carboborations of alkynes and aryl allenes by tris(perfluoro)phenylborane (BCF).[3,4] Furthermore, the Piers' borane-induced catalytic trimerization of alkyl allenes and the dimerization of aryl allenes were reported by Erker and co-workers.[5] These reactions are initiated by the hydroboration of the allene. When introducing $HB(C_6F_5)_2$ as a highly electrophilic borane reagent in 1995, Piers and co-workers described the stoichiometric hydroboration of phenylacetylene by this reagent that leads to the corresponding alkenylborane.[6] We herein report the unexpected finding that the reaction of Piers' borane with an excess of phenylacetylene yields *cis*-2-boryl-1,3,3a,5-tetraphenyl-tetrahydropentalene **1a** (Scheme 1).

Tetrahydropentalenes are frequently used as ligands in transition-metal catalyzed reactions. Examples are the rhodium-catalyzed 1,2- and 1,4-addition of boronic acids to imines and enones.[7] Recently, a chiral bisborane, synthesized via double hydroboration of a tetrahydropentalene with Piers' borane was

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Scheme 1. Formation of *cis*-2-boryl-1,3,3a,5-tetraphenyl-tetrahydropentalene **1a** upon reaction of Piers' borane with five equivalents phenylacetylene. The yield was determined by NMR with trimethoxybenzene as internal standard. The yield of the isolated product is given in parenthesis.

used as the catalyst in the enantioselective metal-free hydrogenation of imines.[8] The synthesis of these tetrahydropentalenes requires a multistep procedure starting from octahydro-pentalenediol or 1,5-cyclooctadiene.[7] Furthermore, the rhodium-mediated formation of hydropentalenyl complexes from terminal alkynes and the palladium-induced cyclotetramerization of acetylenes have been reported.[9] However, the transition-metal free tetramerization of alkynes is to the best of our knowledge unprecedented. Upon reaction of Piers' borane with five equivalents of phenylacetylene at r.t. in DCM, **1a** is obtained after two days in an in situ yield of 56% as determined by NMR. We were not able to detect a diastereomer of **1a**. Subsequently, **1a** was isolated in 41% yield upon crystallization from *n*-hexane and fully characterized. Furthermore, crystals suitable for single-crystal X-ray diffraction (SCXRD) were grown from a saturated *n*-hexane solution. The molecular structure derived from SCXRD supports the structural assignment and confirms the *cis*-relationship of the substituents at the bridge-head positions (Figure 1).

Notably, the reaction also takes place if Piers' borane is reacted with two equivalents phenylacetylene. In this case, hydroboration of the phenylacetylene is observed, followed by the slow formation of **1a** while unreacted alkenylborane remains.[10] The reaction is not limited to phenylacetylene as the substrate: Treatment of alkynes **2b–i** with Piers' borane furnishes the cis-2-boryl-1,3,3a,5-tetra-aryl-tetrahydropentalenes **1b–i** in NMR yields ranging from 32%–55% (Scheme 2).
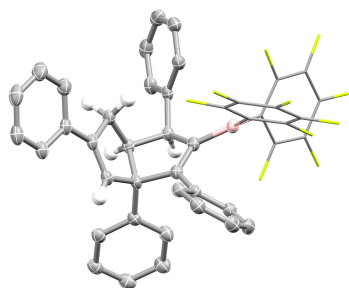
Erker and co-workers demonstrated that boranes with perfluorophenyl substituents can be engaged in transition-

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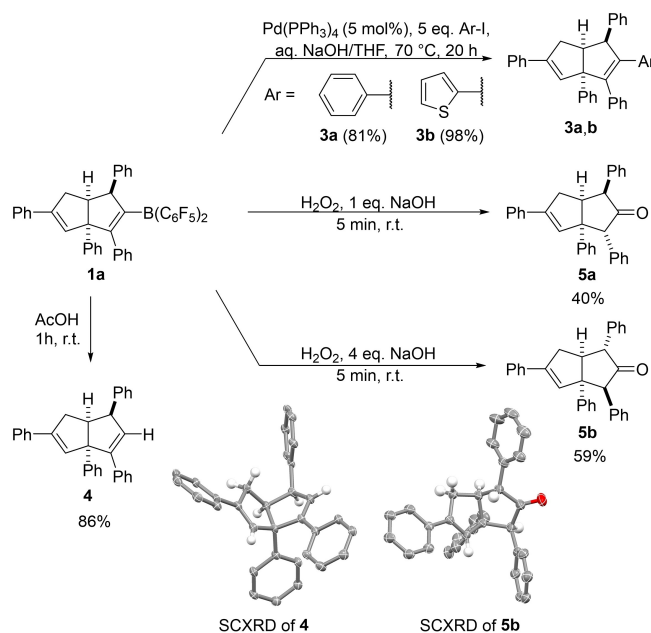European Chemical
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Figure 1. Molecular structure of cis-2-boryl-1,3,3a,5-tetraphenyl-tetrahydro-pentalene **1 a** derived from SCXRD (50% probability ellipsoids, all hydrogens attached to phenyl rings are omitted and C_6F_5 rings are shown in stick representation for clarity). Selected bond lengths and angles: C1–C2: 1.533(2) Å, C2–C3 1.357(2), C3–C3a 1.542(2) Å, C3a–C4 1.513(2) Å, C4–C5: 1.338(3) Å, C5–C6: 1.509(3) Å, C2–C6a: 1.535(3) Å, C6a–C1: 1.540(2) Å.
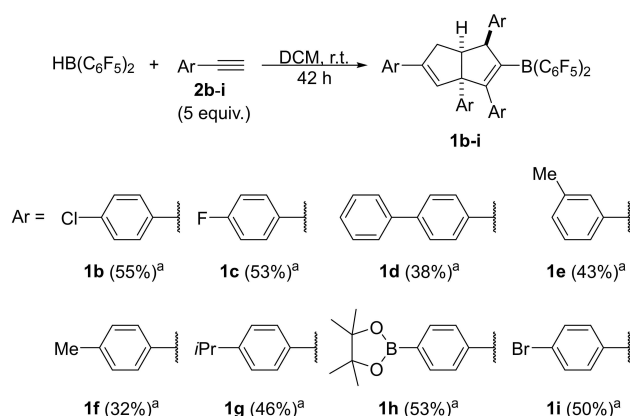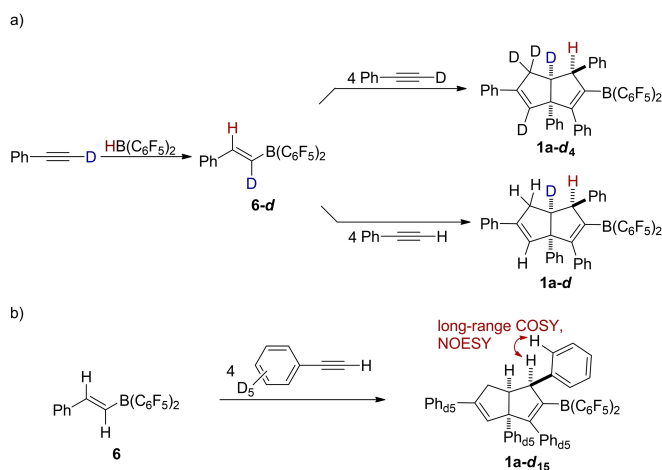

Scheme 2. Tetramerization of aryl allenes by Piers' borane (a) yields determined by ^1H NMR with trimethoxybenzene as internal standard. The yields have an estimated error of +/−5% (see Supporting Information for details).

Scheme 3. Follow-up reactivity of **1 a** in a Suzuki-Miyaura coupling, oxidations, and protodeborylation (yields of isolated products given). The insets show the molecular structure for **4** and **5 b** derived from SCXRD analysis (all hydrogens attached to phenyl rings are omitted for clarity).

Scheme 4. a) Isotope labeling experiments that reveal the position of hydrogen from Piers' borane and that of the initially hydroborated phenyl-acetylene in the final product. b) NMR experiment that disclosed the position of the non-deuterated phenyl moiety of **6** in the final product **1 a**-d_{15}. Deuterium incorporation in the indicated position in each case was at least 88%, as determined by ^1H NMR.

metal catalyzed coupling reactions.[3c,e,5c] To prove that **1 a** is a suitable substrate for a Suzuki-Miyaura coupling, we reacted **1 a** with phenyl iodide and 2-iodothiophene in the presence of catalytic amounts tetrakis(triphenylphosphine) palladium. This allowed us to isolate the penta-aryl-tetrahydropentalenes **3 a** and **3 b** in very good yields (Scheme 3). Furthermore, **1 a** can be protodeborylated by the addition of acetic acid at room temperature yielding the tetrahydropentalene **4** in very good yield (Scheme 3). The oxidation of **1 a** with H_2O_2 and NaOH leads to the corresponding ketones **5 a** and **5 b**. The diastereoselectivity of this reaction can be controlled by the amount of NaOH added. Both products were isolated as single diastereomers in moderate to good yields and fully characterized including NOESY NMR (Scheme 3).[5c] The structural assignments of **4** and **5 b** are further supported by SCXRD analysis (Scheme 3).

To elucidate the mechanism of the transformation that leads to the formation of **1 a**, we performed a series of isotope labeling experiments. Hydroboration of deuterated phenyl-acetylene with Piers' borane yielded, as expected, the mono-deuterated alkenylborane **6-d** (Scheme 4a). The reaction of **6-d**

with four additional equivalents of deuterated phenylacetylene lead to the formation of **1 a**-d_4 with protium exclusively in the 1-position of the pentalene core. On the other hand, the reaction of **6-d** with four equivalents non-deuterated phenyl-acetylene led to **1 a**-**d** with deuterium incorporation in the 6a-position. These experiments, therefore, show that the hydrogen of the initial Piers' borane ends up in the 1-position while the hydrogen of the first equivalent of phenylacetylene is incorporated in the 6a-position of **1 a**. Furthermore, the labeling

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experiments suggest that the carbon atoms in the 1- and 6a-positions of **1a** originate from phenylacetylene that was hydroborated in the first step of the reaction. To substantiate this hypothesis, we reacted alkenylborane **6** with four equivalents of phenylacetylene bearing fully deuterated phenyl rings (Scheme 4b). As a result, all aromatic ¹H NMR signals except those originating from **6** could be suppressed. This enabled us to determine the position of the phenyl moiety of **6** in the product **1a-d_{15}** by long-range COSY and NOESY NMR. This experiment revealed that the phenyl moiety of the alkenylborane which is formed upon initial hydroboration eventually ends up in the 1-position of the final product **1a**.

The position of the first equivalent of phenylacetylene in the final product suggests a reaction that consists of an initial hydroboration and four 1,2-carboborations followed by electrocyclic ring closure of the formed octatetraene.[11,12] Therefore, we investigated the initial steps computationally at the PCM(DCM)-revDSD-PBEP86-D4/def2-QZVPP//PCM(DCM)-PBEh-3c level of theory (Figure 2).[13–16] Furthermore, we considered the barrier for a 1,1-carboboration. According to the computations, the exergonic hydroboration of phenylacetylene by Piers'

borane via **TS₆** requires a Gibbs free energy of activation of 9.0 kcal mol⁻¹. The 1,2-carboboration of phenylacetylene by alkenylborane **6** is asynchronous: The formation of the C–B bond is further advanced in the transition state structure (see inset in Figure 2). This is certainly a result of the high Lewis acidity of **6** and explains the preference of transition state **TS₆/₇** over **TS'**. In the latter, the positive charge arising as a result of asynchronous bond formation is not stabilized by a phenyl substituent. Consequently, the 1,2-carboboration should lead to the diene **7** in which the phenyl substituents are in a 1,3-distance. The barrier for the 1,1-carboboration is computed to be 4.8 kcal mol⁻¹ higher than the one for the 1,2-carboboration

We note that the computed transition state structure for the 1,1-carboboration is structurally similar to the one reported by Grimme and Erker for the 1,1-carboboration of alkynes by BCF.[3b] While the barrier for the 1,2-carboboration via **TS₆/₇** is surmountable at r.t., the computed barriers for the carboborations via **TS'** (28.8 kcal mol⁻¹) and **TS₁,₁-carboboration** (27.4 kcal mol⁻¹) are conflicting with the experimental observation that the tetramerization occurs at ambient conditions. The findings that the formation of **1a** is also observed when Piers' borane is
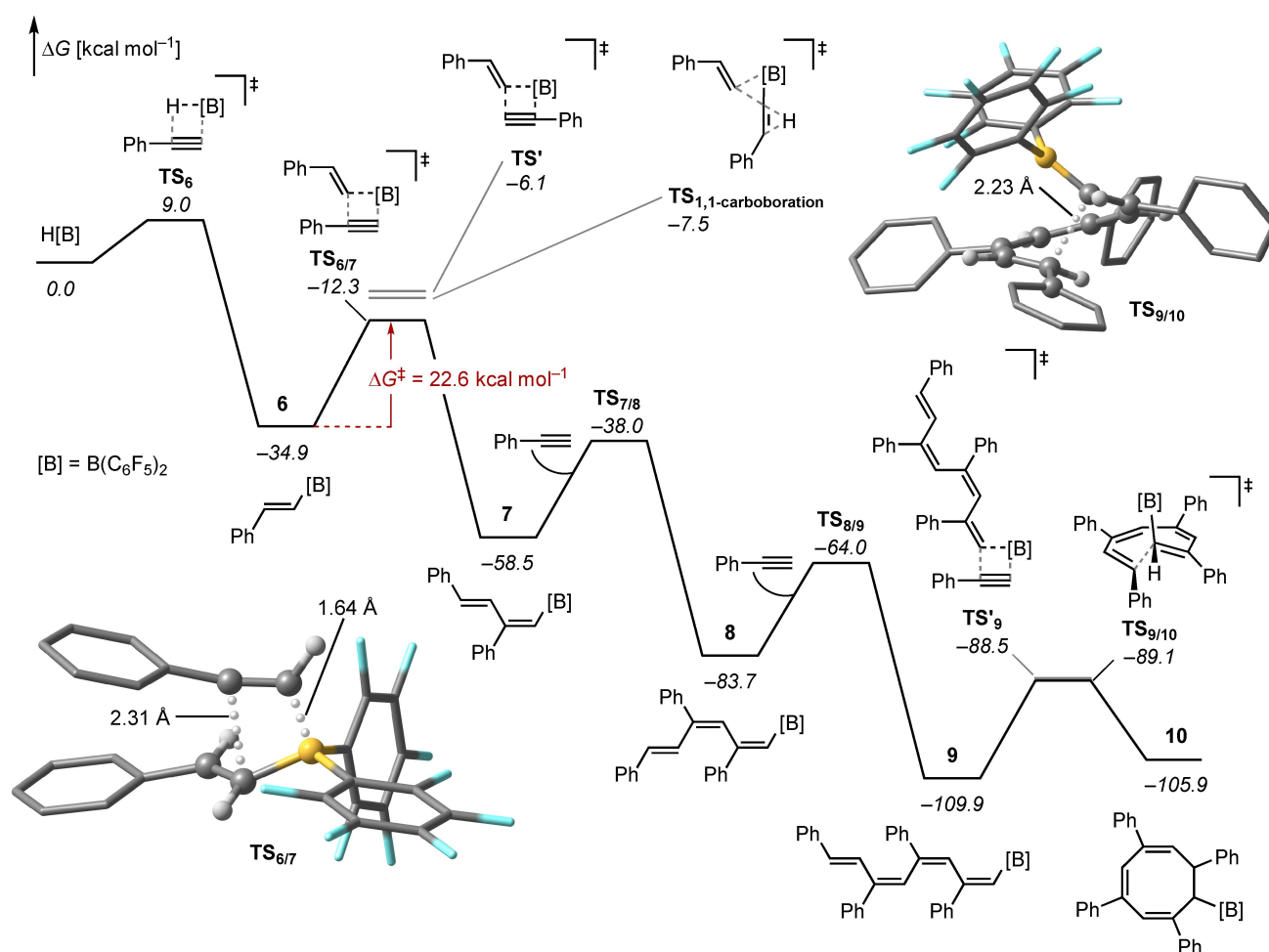
Figure 2. Schematic PES of the formation of the cyclooctatriene **10** and barriers for the 1,2- and 1,1-carboboration of phenylacetylene by **6** computed at PCM(DCM)-revDSD-PBEP86-D4/def2-QZVPP//PCM(DCM)-PBh-3c. The insets show the computed transition state structures of the 1,2-carboboration leading to **7** and the 8π-electrocyclization leading to cyclooctatriene **10**.

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doi.org/10.1002/chem.202104254

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reacted with only two equivalents phenylacetylene and that no intermediate except alkenylborane **6** can be detected by ^{1}H NMR reaction monitoring further indicate that this initial 1,2-carboboration is rate-determining.[10] Indeed, the computed barriers for the subsequent 1,2-carborations (**TS$_{7/8}$** and **TS$_{8/9}$**) are lower than the one for the initial carboboration. An 8π-electrocyclization of the tetraene **9** via **TS$_{9/10}$** yields then the cyclooctatriene **10**. The computed barrier of 20.8 kcal mol^{-1} for the 8π-electrocyclization of **9** does not differ substantially from the barrier obtained experimentally for the electrocylization of unsubstituted octatetraene (17.0 kcal mol^{-1}) and permits this step to occur readily at r.t.[17] Although a fourth 1,2-carbobora-tion via **TS'$_9$** is slightly disfavored compared to the electro-cyclization via **TS$_{9/10}$**, both transition states are close in energy so that further oligomerizations could be a possible side reaction. The sequence of 1,2-carborations and electrocycliza-tion would locate the first equivalent of phenylacetylene in the relative position to the boryl substituent that was deduced from the isotope labeling experiments. The thermal and photo-chemical rearrangements of cycloocatrienes to semibullvalenes were reported.[18,19] An analogous $_\pi4_a + _\pi2_a$ rearrangement of **10** would lead to tricycle **11** (Scheme 5).

A vinylcyclopropane-cyclopentene rearrangement of **11** would form **12**. These rearrangements usually require high activation energies.[18,20] However, it was shown that Lewis acids can lower the barrier for vinylcyclopropane-cyclopentene rearrangements significantly.[21] Thus, we assume that this transformation is catalyzed by Lewis acidic boranes present in the reaction. Additionally, the electrophilic perfluorophenyl substituted boranes could serve as one-electron acceptors and promote the rearrangement from **10** to **11** via a (di)radical pathway.[22] Finally, a simple proton shift can convert **12** into the experimentally observed product **1a**. According to our computations at PCM(DCM)-revDSD-PBEP86-D4/def2-QZVPP// PCM(DCM)-PBEh-3c, formation of **1a** from **10** is exergonic by 28.2 kcal mol^{-1}. We note that the relative position of the phenyl substituents in **1a** that would result from the proposed $_\pi4_a + _\pi2_a$ rearrangement and the vinylcyclopropane-cyclopentene rear-rangement agrees with the experimentally determined one. However, it must be stressed that other reaction pathways

cannot be excluded at present and further computational and experimental investigations to clarify the mechanistic details of the formation of **1a** are ongoing.

In summary, we have documented the unprecedented tetramerization of simple arylacetylenes by Piers' borane. We expect this finding to stimulate the development of new methods for organic synthesis that rely on the oligomerization of alkynes by Lewis acidic boranes.

Experimental Section

See the Supporting Information for details.

Deposition Numbers 2107142, 2121641 and 2124445 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
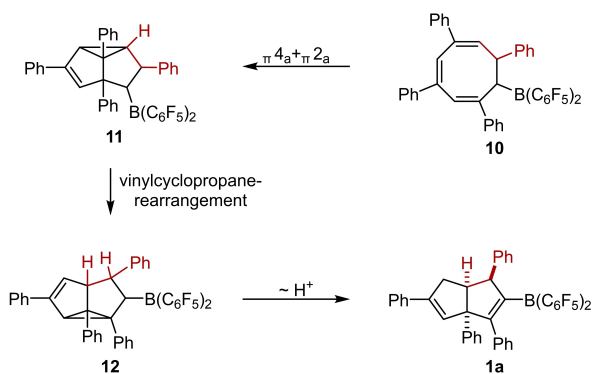
Conflict of Interest

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.

Scheme 5. Proposed mechanism for the formation of **1a**. The first equivalent alkenylborane, whose position was determined by isotope labeling experiments, is highlighted in red.

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