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Indene formation upon borane-induced cyclization of arylallenes, 1,1-carboboration, and retro-hydroboration†

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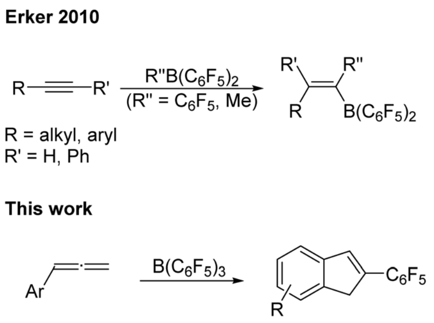
We herein report the reaction of arylallenes with tris(pentafluorophenyl)borane that yields pentafluorophenyl substituted indenes. The tris(pentafluorophenyl)borane induces the cyclization of the allene and transfers a pentafluorophenyl ring in the course of this reaction. A Hammett plot analysis and DFT computations indicate a 1,1-carboboration to be the C–C bond-forming step.

In 2010, Erker and co-workers reported that the reaction of the strongly Lewis acidic tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) with terminal alkynes leads to a 1,1-carboboration of the alkyne.[1] The substrate scope of the 1,1-carboboration was extended to phosphinyl substituted alkynes, yielding alkenyl-bridged frustrated Lewis pairs.[2] Furthermore, the 1,1-carboboration of internal alkynes with concomitant C–C cleavage was demonstrated.[3,4] More recently, Melen *et al.* reported the 1,2-carboboration of allenyl ketones.[5]

We found now that the reaction of $B(C_6F_5)_3$ with phenylallene **1** leads to the formation of the pentafluorophenyl-substituted indene **2** (Scheme 1).[6] Our initial finding was that the addition of **1** to a solution of $B(C_6F_5)_3$ in dichloromethane-d_2 (DCM-d_2) leads to the formation of indene **2** in 48% NMR-yield within 45 minutes (Scheme 2).

Hence, the $B(C_6F_5)_3$ induces a ring closure and transfers a pentafluorophenyl ring to the allene.[7] As a side product of this reaction, we observed the allylborane **3** that is likely formed by hydroboration of the phenylallene **1**.[8] Besides, minor amounts of a vinylborane, originating from the hydroboration of the internal double bond, and a 2-boryl-hexa-1,5-dien, formed by Piers' borane induced dimerization of the allene, were detected (for details, see the ESI†). The detection of **3** gives a direct hint to the intermediate formation of Piers' borane $HB(C_6F_5)_2$ in the course of the reaction.[9] Accordingly, the reaction constitutes a formal exchange of a pentafluorophenyl group of the $B(C_6F_5)_3$ with hydrogen. The reaction was subsequently performed on a preparative scale and the indene **2** was isolated and fully characterized. The structural assignment is further supported by SCXRD (Scheme 2). We then investigated the scope of this transformation by reacting different aryl allenes with $B(C_6F_5)_3$. As the hydroboration observed in the initial experiment consumes some of the allene, these reactions were performed with two equivalents of the allene. Under these conditions, **2** was isolated in 68% yield with respect to $B(C_6F_5)_3$, the limiting reagent (Scheme 3). The same reaction with one equivalent phenylallene and norbornene as sacrificial olefine to capture Piers' borane yielded **2** in 58% yield. The benzindene **4** is obtained in 65% yield from the reaction of 1-naphthylallene with $B(C_6F_5)_3$. However, it was isolated as a mixture of isomers that differ regarding the position of the benzylic double bond. Likewise, the reaction of *p*-tolylallene and *p*-(isopropyl)phenylallene gives the indenes **5** and **6** as a mixture of regioisomers.



Scheme 1 The context of this work: the 1,1-carboboration of alkynes described by Erker and the borane-induced ring closure with concomitant aryl group transfer described herein.

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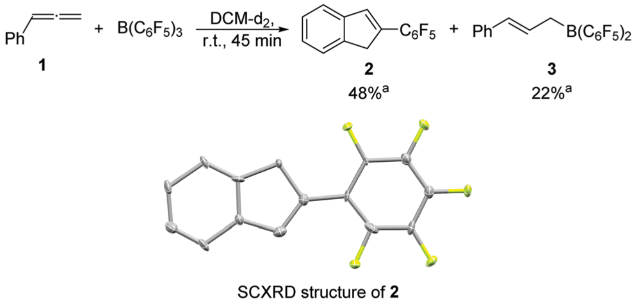
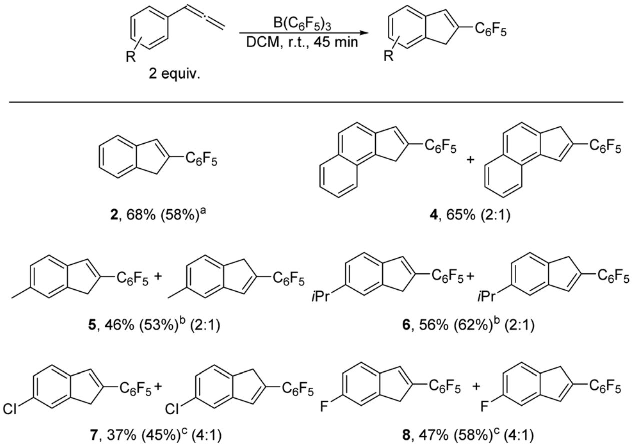


Scheme 2 Formation of the pentafluorophenyl-substituted indene **2** upon the reaction of **1** with $B(C_6F_5)_3$. [a]Yields determined by qNMR with 1,3,5-trimethoxybenzene as internal standard. The inset shows the molecular structure of **2** derived from SCXRD (50% probability ellipsoids, all hydrogen atoms are omitted for clarity).



Scheme 3 Scope of the $B(C_6F_5)_3$ mediated formation of indenes from allenes. Yields of products isolated by column chromatography are given. (a) With one equivalent phenylallene and one equivalent norbornene. (b) Reaction temperature 0 °C. (c) Oil bath temperature 60 °C.

A better yield was obtained when the reactions with these substrates were run at 0 °C, presumably because of side reactions at r.t. In contrast, the reactions with *p*-(chloro)phenylallene and *p*-(fluoro)phenylallene required an elevated reaction temperature to give **7** and **8** in moderate yields. These findings indicate that electron-rich arylallenes undergo a faster cyclization whereas electron-withdrawing substituents slow down the reaction.

The effect of the substituents on the phenyl ring on the reaction rate was further assessed by a Hammett analysis (Fig. 1).[10] The negative slope of the Hammett plot and the rho value of −3.9 ± 0.7 indicate that in the rate-determining transition state of this reaction positive charge is built up in the benzylic position of the arylallene.

The increased reactivity of electron-rich allenes was used for a cyclization with a less Lewis acidic borane. The reaction of *p*-(isopropyl)phenylallene with $MeB(C_6F_5)_2$ leads to cyclization of the allene and transfer of the methyl group (Scheme 4). However, the formation of methylindene **9** required a prolonged reaction time.

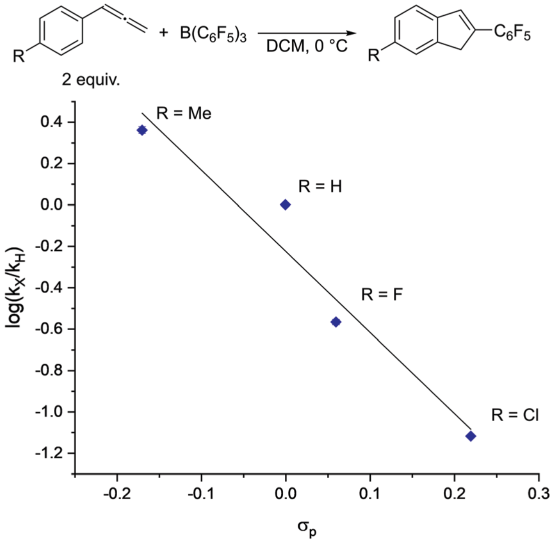
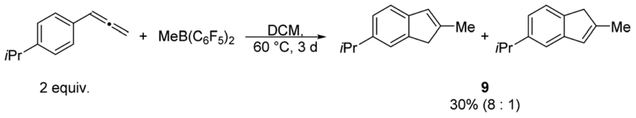


Fig. 1 Hammett plot analysis of the $B(C_6F_5)_3$- mediated formation of indenes from aryl allenes. Note that only the major isomer is shown in the scheme.



Scheme 4 Formation of the methyl indene 9 upon reaction of *p*-(isopropyl)phenylallene with $MeB(C_6F_5)_2$.

The mechanism of the $B(C_6F_5)_3$-mediated indene formation was further investigated computationally by DFT at the revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c level of theory (Fig. 2).[11–13] As zwitterionic intermediates are likely involved in the reaction, the SMD solvent model for DCM was used for the structure optimizations and the single point computations.[14] We assume that the reaction commences with the addition of $B(C_6F_5)_3$ to the π-system of **1**. This step yields the zwitterion **INT-1**. The positive charge in this intermediate is stabilized by allyl and benzyl resonance. An intramolecular Friedel–Crafts alkylation *via* **TS-2** closes the five-membered ring of the indene core. We further assume that an intermolecular proton shift leads to a re-aromatization and the intermediate **INT-3** (Scheme 5). However, all attempts to optimize the structure of **INT-3** resulted in a pentafluorophenyl transfer and lead to **INT-4**. Relaxed potential energy surface scans further showed that the pentafluorophenyl transfer is a barrierless process. This finding agrees with computational studies of the 1,1-carboboration of alkynes by Erker, Grimme, and co-workers that showed that once a carbocation is formed in α-position to the $B(C_6F_5)_3$ moiety, the pentafluorophenyl transfer is barrierless.

A retro-hydroboration, *i.e.* the liberation of $HB(C_6F_5)_2$ from **Int-4**, forms product **2**. According to the computations, this step requires only a moderate activation energy of 16.7 kcal mol^{-1}. Notably, the retro-hydroboration is computed to be exergonic by 2.2 kcal mol^{-1}. According to the computations, **TS-1**, the

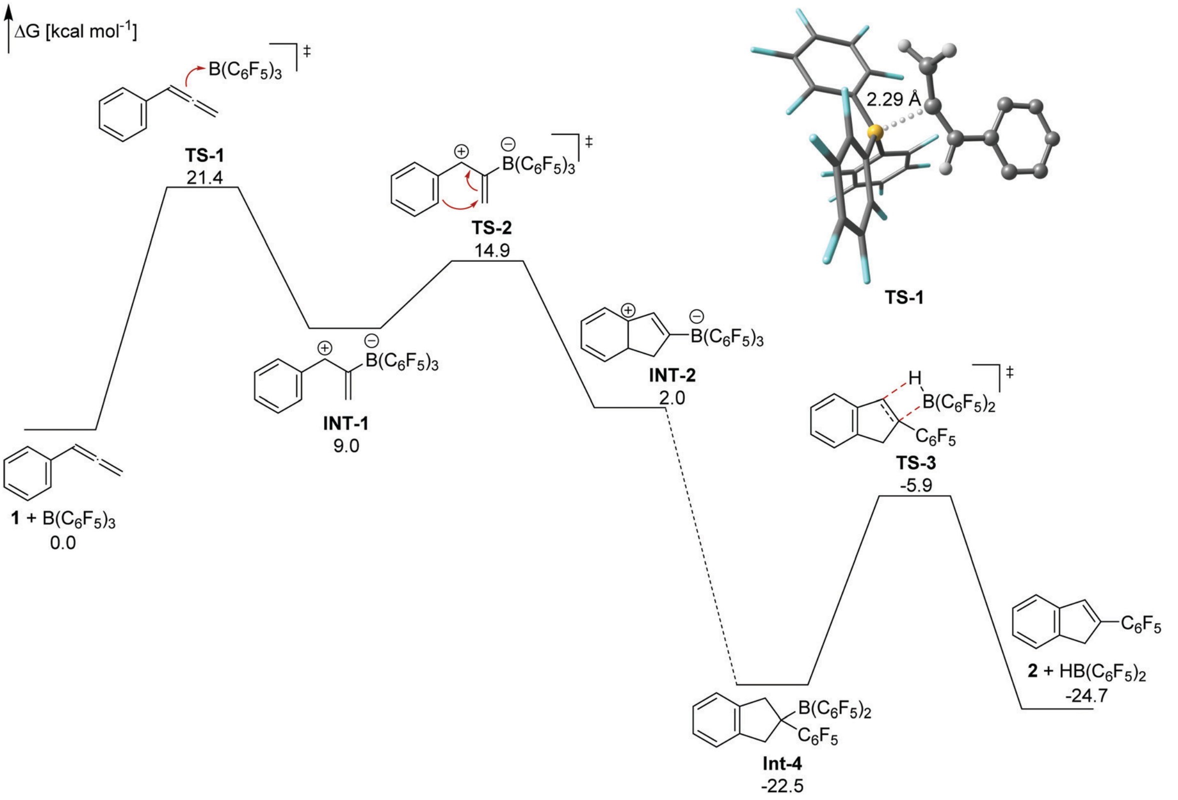
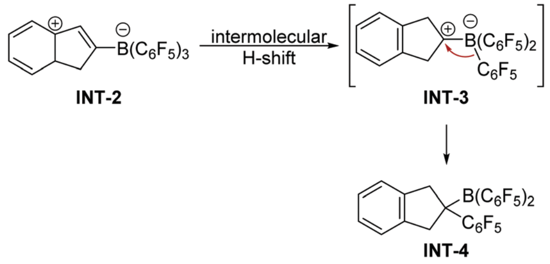


Fig. 2 Gibbs free energies of the $B(C_6F_5)_3$-mediated indene formation computed at the revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c level of theory. The SMD solvent model for DCM was used for the structure optimizations and the single point computations. The inset shows the optimized structure of **TS-1**.



Scheme 5 Proposed mechanism for the pentafluorophenyl transfer.

addition of the phenyl allene to $B(C_6F_5)_3$, is the rate-determining transition state. In this transition state, a positive charge is built up in the benzylic position that is stabilized by electron-donating groups in the para position. Thus, the computations are in favorable agreement with the Hammett analysis. In summary, we have documented that the reaction of arylallenes with $B(C_6F_5)_3$ leads to pentafluorophenyl substituted indenes. A plausible mechanistic scenario consists of a $B(C_6F_5)_3$-induced cyclization, a pentafluorophenyl transfer, and a retro-hydroboration. This reaction is a rare example of a metal-free C_{sp^2}–C_{sp^2} bond formation.[15] The results reported herein might inspire the development of synthetic methods that rely on 1,1-carboboration and retro-hydroboration reactions.

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Conflicts of interest

There are no conflicts to declare.

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