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Carbon−Carbon Bond Activation by 1,1-Carboboration of Internal Alkynes

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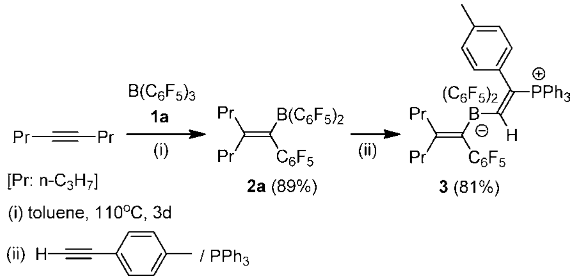
Abstract: Internal alkynes undergo 1,1-carboboration reactions upon treatment with boranes $RB(C_6F_5)_2$ ($R = C_6F_5$, CH_3) to yield trisubstituted alkenylboranes. These products can be used as substrates in Pd-catalyzed cross-coupling reactions.

Developing new activation protocols for the chemical utilization and modification of otherwise unactivated strong σ bonds is a central task in experimental chemistry. In the past several years, a variety of convincing solutions have been developed, for example, for C−H bond activation[1] and quite recently even for metal-free splitting of dihydrogen.[2] In contrast, the chemical repertoire for selectively attacking unactivated carbon−carbon single bonds is still small.[3] We here report on a surprisingly simple C−C bond-activation process that takes place upon treatment of internal alkynes with a variety of strongly electrophilic boranes, and we demonstrate that the resulting new borane-substituted frameworks can be utilized for additional carbon−carbon bond formation to eventually yield tetrasubstitued alkenes.

We found that the borane $B(C_6F_5)_3$ (**1a**)[4] reacts cleanly with 4-octyne in toluene solution at elevated temperature. After 3 days at reflux temperature, we isolated the 1,1-carboboration product **2a** in 89% yield. NMR analysis revealed that one C(sp)−C(sp^3) carbon−carbon single bond had been broken in the course of the reaction and that the corresponding *n*-propyl group had migrated to the other alkyne terminus. Additionally, in the course of this reaction, a C_6F_5 substituent was transferred from boron to carbon.[5] The $^1H/^{13}C$ NMR spectra of **2a** feature the typical signals of a geminal pair of *n*-propyl groups. Compound **2a** shows a typical ^{11}B NMR signal (at δ 60.9) of a tricoordinated $RB(C_6F_5)_2$ Lewis acid. The structural characterization of **2a** was achieved after derivatization. Treatment of the 1,1-carboboration product **2a** with a 1:1 mixture of triphenylphosphine/*p*-tolylacetylene gave the typical *trans*-1,2-addition product of the resulting P/B frustrated Lewis pair to the terminal alkyne[6] to yield **3** (see Scheme 1 and Figure 1). Compound **3** was characterized by X-ray crystal structure analysis. The structure contains the tetracoordinated olefinic $(n\text{-}C_3H_7)_2C{=}C(C_6F_5)[B]$ unit that was typically obtained by 1,2-alkyl migration proceeding in accord with B−C and $C{-}C_6F_5$ bond formation in the 1,1-carboboration reaction sequence.[5]

Scheme 1



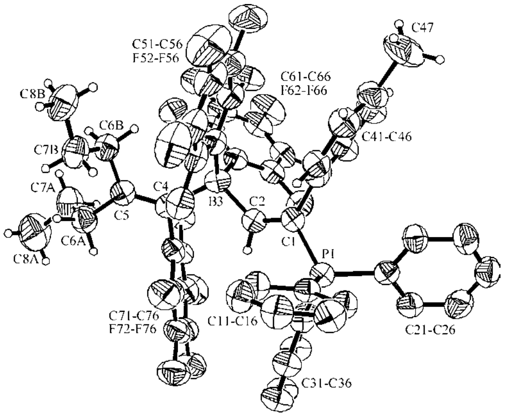


Figure 1. Molecular structure of compound **3** (hydrogens at the phenyl groups have been omitted for clarity; thermal ellipsoids are shown at the 50% probability level).

We then reacted tolane with $B(C_6F_5)_3$. Clean 1,1-carboboration took place in a slow reaction in toluene at 110 °C with 1,2-phenyl migration, giving **2b** in 88% yield. The product shows a typical pair of ^{19}F NMR spectroscopic sets of resonances in a 2:1 ratio for the $-B(C_6F_5)_2$ moiety and the migrated $-C_6F_5$ substituent. This product was directly characterized by X-ray crystal structure analysis [B1−C2, 1.559(3) Å; B1−C2−C3, 122.0(2)°; C2−C3, 1.364(3) Å; see Figure 2 left]. Bis(*p*-tolyl)acetylene reacted analogously with $B(C_6F_5)_3$. We isolated the corresponding 1,1-carboboration product **2c** as a yellow solid in 63% yield.

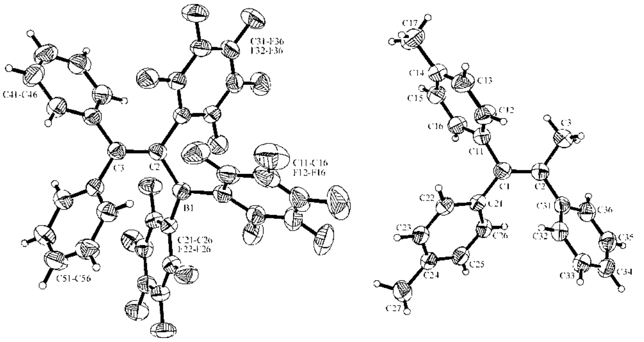


Figure 2. Molecular structures of (left) **2b** and (right) **4b** (thermal ellipsoids are shown at the 50% probability level).

The reaction is not limited to transfer of a C_6F_5 group from boron to carbon. Treatment of readily available $CH_3B(C_6F_5)_2$ (**1b**)[7] with bis(*p*-tolyl)acetylene at 125 °C showed that the 1,1-carboboration of the internal alkyne was achieved with selective migration of the methyl group from boron to the former acetylene carbon in the course of the slow C−C bond-activation process to yield **2d**, which was isolated in 49% yield (see Scheme 2).

Alkenylboron compounds are widely used in organic synthesis,[8] photochemistry,[9] and coordination chemistry.[10] In particular, they

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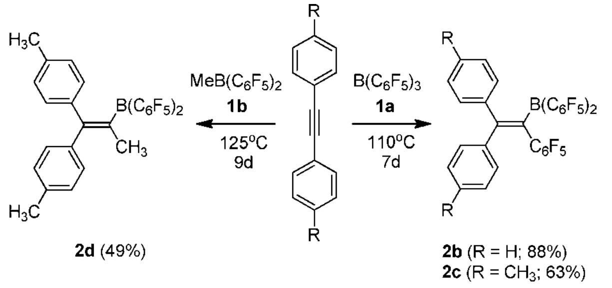
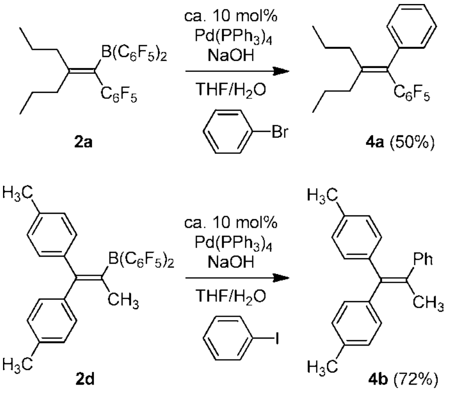
Scheme 2



are used as alkenyl reagents in coupling reactions for the preparation of substituted alkenes.[8a] The products **2** all contain a reactive boryl substituent. The newly formed alkenylborane moiety in these compounds can be synthetically utilized for subsequent carbon−carbon bond formation in a Pd-catalyzed reaction that is related to Suzuki−Miyaura-type coupling.[8c] Thus, we treated the 1,1-carboboration product **2a** with phenyl bromide at 70 °C in aqueous THF in the presence of sodium hydroxide base and ∼10 mol % $Pd(PPh_3)_4$ catalyst. This led to C−C coupling that resulted in the formation of tetrasubstituted olefin **4a**, which we isolated in 50% yield. Similarly, the Pd-catalyzed arylation of the 1,1-carboboration product **2d** with phenyl iodide gave the cross-coupled product **4b** in good yield (see Scheme 3). X-ray crystal structure analysis of **4b** showed the geminal pair of *p*-tolyl substituents at C1 of the double bond, which originated from the 1,1-carboboration reaction of bis(*p*-tolyl)acetylene with **1b**, and the phenyl and methyl groups on C2 [C1−C2, 1.349(2) Å; ∑deg(C1) = 360°; ∑deg(C2) = 360°; see Figure 2 right].

Scheme 3



1,1-Carboboration reactions had been observed to rapidly proceed upon treatment of various main-group- or transition-metal-substituted alkynes with boranes,[5,11] but they have rarely been described in cases of simple organic acetylenes.[12,13] However, this unique topology of the 1,1-carboboration sequence is especially attractive starting from simple internal alkynes that bear conventional organic substituents.

The well-defined and very selective rearrangement sequence observed here leads to trisubstituted alkenylboranes that, as we have shown, represent interesting new boron Lewis acids. In addition, these products are amenable to subsequent utilization of the boryl functionality for carbon−carbon bond formation. Such new variants of the 1,1-carboboration reaction[14] are well-suited for opening new general pathways in carbon−carbon bond-activation chemistry.

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Supporting Information Available: Text and figures giving further experimental and spectroscopic details and CIF files giving crystallographic data for **2b**, **3**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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