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Carbon–Carbon Bond Cleavage by Strongly Electrophilic Boranes

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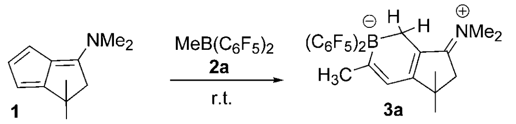
Attack and cleavage of strong unactivated bonds for a selective functionalization of the resulting compounds has been a continuing major challenge and important task in chemistry. While the activation of dihydrogen[1] and subsequently carbon–hydrogen bond activation have been achieved with a large selection of powerful methods,[2–5] the activation and cleavage of carbon–carbon (C−C) bonds has attracted much less attention.[4–7] Methodologically it is to be regarded as problematic. There are classical methods known for the selective cleavage of strong unactivated C−C bonds, such as the ozonolysis cycloaddition/cycloreversion sequence[8,9] or the metal-catalyzed olefin metathesis reaction.[10,11] However, the stage of the development of C−C bond activation does not even come close to that of, for example, C−H activation chemistry. We have now found a C−C bond cleavage reaction that takes place straightforwardly upon treatment of a suitable substrate with strongly electrophilic boranes. The reaction sequence forms two new carbon–boron (C−B) bonds at the expense of the C−C linkage.

We have found that $MeB(C_6F_5)_2$ (**2a**) reacts cleanly with the aminodihydropentalene derivative **1** at room temperature to yield the C−C cleavage product **3a** (Scheme 1). When the two reagents were mixed in pentane at room temperature, a precipitate began to appear after 1 h and we isolated the product **3a** in greater than 60 % yield after two days. It was characterized spectroscopically, by elemental analysis, high-resolution mass spectrometry, and by X-ray diffraction. The X-ray crystal structure analysis of **3a** (Figure 1) shows that the boron atom has cleaved a C=C bond of the substrate and formed two new boron–carbon linkages (B6−C5 1.658(3), B6−C7 1.623(4) Å). The boron insertion was coupled with a selective migration of the methyl group from the boron atom to the carbon atom to yield the observed methyl-substituted borata-cyclohexadiene subunit found in **3a**. This is part of a doubly conjugated iminium salt (N1−C3 1.313(3), C4−C9 1.366(3), C8−C7 1.349(3) Å) inside the zwitterionic heterobicyclic framework of **3a**.



Scheme 1. Reaction of dimethylaminodihydropentalene derivative **1** with the borane reagent $MeB(C_6F_5)_2$.

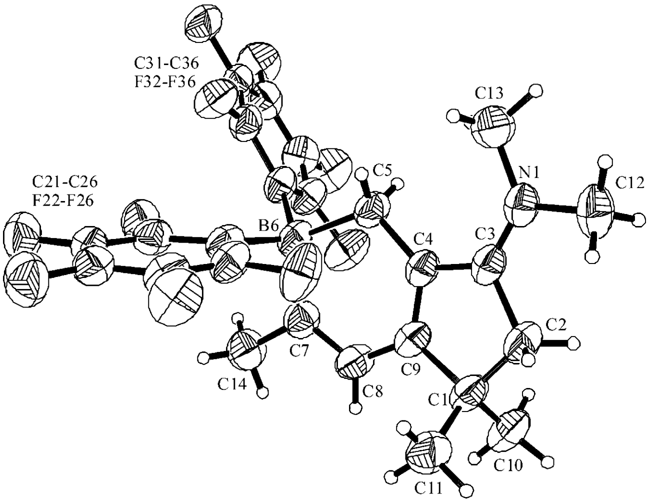


Figure 1. A view of the molecular structure of **3a**.

In solution, compound **3a** features a ^{11}B NMR signal at $\delta = -14.1$ ppm and a set of typical "borate-C_6F_5" ^{19}F NMR resonances [$\Delta\delta$ (p,m-F) = 2.8 ppm]. It shows the 7-CH_3 ^{1}H NMR signal at $\delta = 2.41$ ppm and ^{13}C NMR signals of the

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X-ray structure analyses.

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conjugated π system at $\delta = 191.5$ (C7), 188.6 (C9), 181.3 (C=N), 128.9 (C4), 123.4 ppm (C8).

The related strongly Lewis acidic borane $PhCH_2CH_2B(C_6F_5)_2$ is readily available by hydroboration of styrene with "Piers' borane" $[HB(C_6F_5)_2]$.[12] The borane **2b** reacts analogously with the aminodihydropentalene substrate **1** by C=C cleavage/boron insertion to yield the product **3b** (isolated yield 58 %), which was also characterized by X-ray diffraction (see Figure 2, further details see the Supporting Information).

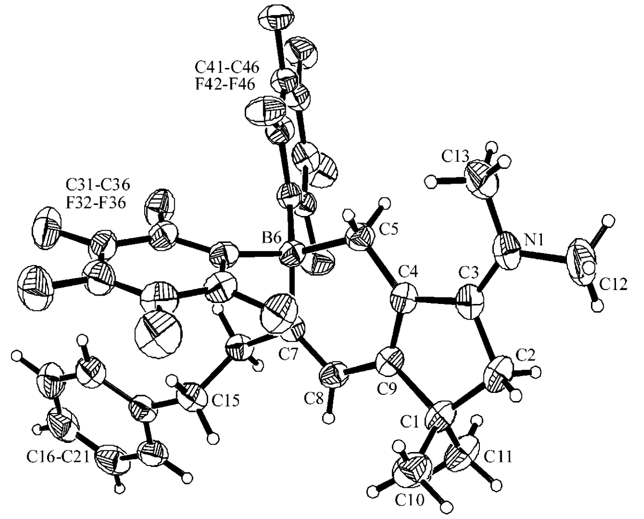
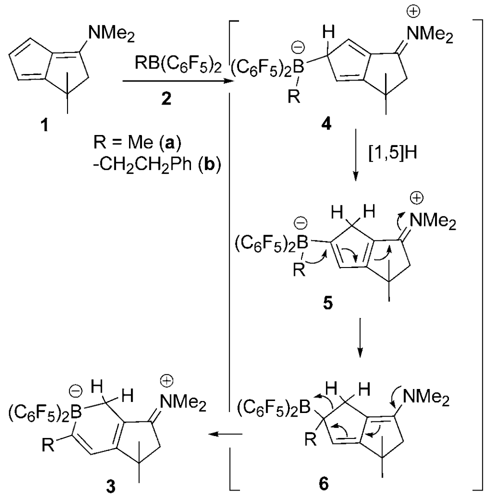


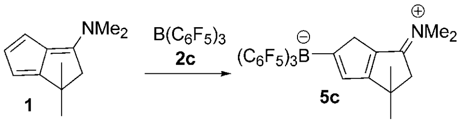
Figure 2. Molecular structure of **3b**. Selected bond lengths [Å] and angle [°]: B6–C5 1.659(3), B6–C7 1.621(3), C7–C8 1.348(3), C8–C9 1.439(3), C9–C4 1.369(3), C4–C3 1.427(3), C3–N1 1.321(3); C7-B6-C5 112.6(2).

The formation of the C=C cleavage product **3** can be rationalized by the reaction sequence described in Scheme 2. The sequence is initiated by boron Lewis acid addition to the substrate **1** to generate **4**. A subsequent 1,5-hydrogen shift inside the substituted cyclopentadiene leads to the zwitterion **5**. In this intermediate the ring position adjacent to the boron atom becomes activated for nucleophilic attack by conjugation with the iminium ion functionality. Consequently, nucleophilic R-migration from boron to carbon can now take place to give **6**. The topological reversal of the last step opens a pathway for the migration of the C5 alkyl group to boron with concurrent cleavage of the C7–C5 carbon–carbon bond to yield the observed product **3**.



Scheme 2. A possible mechanism for C=C bond cleavage by $RB(C_6F_5)_2$ boranes.

This pathway leading to C=C cleavage of **1** is supported by the direct observation of the intermediate **5b** ($R = CH_2CH_2Ph$) by performing the **1** plus **2b** reaction under similar conditions with direct NMR control and by isolating the related product **5c** from the reaction of the aminodihydropentalene derivative **1** with $B(C_6F_5)_3$ (**2c**) (Scheme 3; compound **5b** gave ca. 90 % pure product **3b** upon keeping the NMR sample for 4 h at 55 °C; compound **5c** was isolated in 85 % yield, for details of its characterization see the Supporting Information). Compound **5c** was characterized by X-ray diffraction (see Figure 3). It shows a typical conjugated zwitterionic bicyclic framework (B1–C6 1.623(5), C5–C6 1.520(4), C6–C7 1.364(4) Å) with a pair of anellated five-membered rings. We assume that the lower nucleophilicity of the $B{-}C_6F_5$ unit in this case has prevented the rapid sub-



Scheme 3. Reaction of dimethylaminodihydropentalene derivative **1** with borane reagent $B(C_6F_5)_3$.

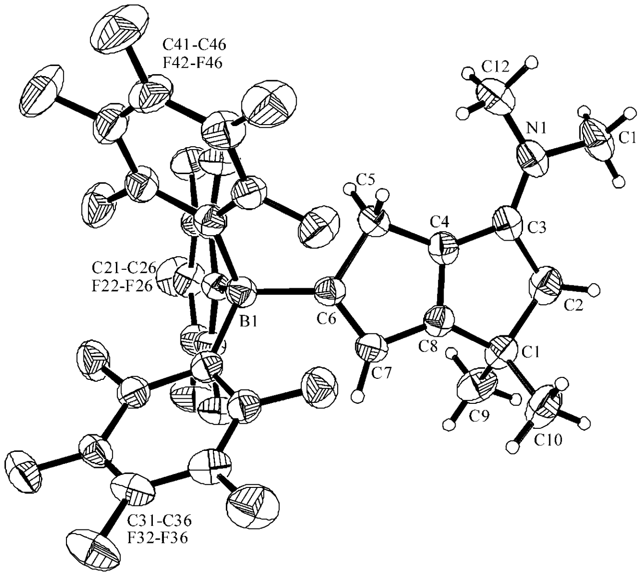


Figure 3. Molecular structure of **5c**.

sequent reaction of **5c** to its ring-enlarged isomer (**3c**) and hence has allowed its isolation.

Our new reaction sequence formally involves an unprecedented 1,1-carboboration reaction[13–18] of an olefin (**1** → **6**) followed by 1,2-alkyl migration from carbon to boron (**6** → **3**) that eventually results in the cleavage of the C–C bond. Our example shows that the utilization of such unusual reaction patterns with selected substrate families can lead to new reaction types such as the efficient C–C bond activation described in this report.

Experimental Section

Synthesis of compound 3a: $MeB(C_6F_5)_2$ (100 mg, 0.28 mmol) and **1** (53 mg, 0.30 mmol) were dissolved in pentane (10 mL) at room temperature and a yellow-red solid began to precipitate after 1 h. After the reaction mixture had been stirred for 48 h, the solid was isolated by cannula filtration and washed twice with cold pentane (2.5 mL). A solution of the obtained solid in benzene (5 mL) was heated up to 55 °C for 4 h. Removal of all volatiles in vacuo yielded **3a** (93 mg, 62 %) as a red powder. Crystals suitable for X-ray crystal structure analysis were grown from the reaction phase between **1** and $MeB(C_6F_5)_2$ in pentane solution at room temperature. Elemental analysis calcd (%) for $C_{25}H_{20}BF_{10}N$: C 56.10, H 3.77, N 2.62; found: C 55.43, H 3.60, N 2.39. HRMS (ESI) exact mass for $[M+Na]^+$ ($C_{25}H_{20}BF_{10}NNa$): calcd: *m/z* 558.1426, found: *m/z* 558.1423. For more experimental details and complete characterization, see the Supporting Information.

Synthesis of compound 3b: Styrene (40 μL, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. A solution of **1** (65 mg, 0.37 mmol) in pentane (3 mL) was added at room temperature, and after 1 h a yellow-red solid began to precipitate. After the reaction mixture had been stirred for 24 h, the solid was isolated by cannula filtration and washed twice with cold pentane (2.5 mL). A solution of the obtained solid in benzene (5 mL) was heated up to 55 °C for 4 h. Removal of all volatiles in vacuo yielded **3b** (123 mg, 58 %) as a red powder. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **3b** in benzene at room temperature. Elemental analysis calcd (%) for $C_{32}H_{26}BF_{10}N\cdot 0.5\,C_6H_6$: C 64.55, H 4.25, N 2.03; found: C 64.57, H 3.93, N 1.74. For more experimental details and complete characterization of **3b** and involving intermediate **5b**, see the Supporting Information.

Synthesis of compound 5c: $B(C_6F_5)_3$ (100 mg, 0.20 mmol) was dissolved in pentane (6 mL) and stirred for 5 min. A solution of **1** (39 mg, 0.22 mmol) in pentane (3 mL) was added at room temperature and a white precipitate was immediately formed. After the reaction mixture had been stirred for 24 h, the solid was isolated by cannula filtration and washed twice with cold pentane (2.5 mL). Removal of all volatiles in vacuo yielded **5c** (117 mg, 85 %) as a white powder. Elemental analysis calcd (%) for $C_{30}H_{17}BF_{15}N$: C 52.43, H 2.49, N 2.04; found: C 52.48, H 2.40, N 2.08. For more experimental details and complete characterization, see the Supporting Information.

Acknowledgements

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Keywords: boranes · carboboration · C–C activation · ring expansion

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[13] 1,1-Carboboration can typically be observed upon treatment of specifically metal-substituted alkynes with boranes to yield alkenylboranes.[14] In addition, a small number of examples of 1,1-carboboration reactions of simple terminal alkynes has been reported.[15–17]

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