**N-Heterocyclic Carbene-facilitated Condensation of 3-Methylphenylboronic Acid to the Boroxine**

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Dedicated to Professor Heinrich Nöth on the occasion of his 85\(^{th}\) birthday

The adduct of \((3\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3\) with an \(N\)-heterocyclic carbene (NHC = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene) was prepared by reacting 2.5 equiv. of 3-methylphenylboronic acid with 1 equiv. of the NHC. This reaction shows a novel carbene-facilitated condensation of substituted phenylboronic acid monomers. The structure of the compound \((3\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3(\text{NHC})\) (1) has been characterized by \(^1\text{H NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction studies.}

**Key words:** Carbene, Boroxine, Adduct

**Introduction**

Boroxines are formed by dehydration of boronic acids [1]. They are extensively used as flame retardant materials in lithium ion batteries, and as alternatives in Suzuki-Miyaura coupling reagents [2 – 6]. The known protocols for the synthesis of boroxine adducts are chemical dehydration or ligand-facilitated condensation of boronic acid monomers. They easily form adducts with nitrogen-containing ligands due to their Lewis acid character [2, 7 – 12] (with pyridines [13, 14], salen type ligands [15]).

\(N\)-Heterocyclic carbenes are considered as important Lewis bases with strong \(\sigma\)-donor properties but very weak \(\pi\)-acceptor characteristics. These nucleophilic carbenes are used as catalysts and ligands. In addition, they form for example stable adducts with metalloids of metal organic compounds and main group Lewis acids [16 – 19].

However, to the best of our knowledge, there is still no report of a carbene boroxine adduct. Herein, we present the synthesis and characterization of an \(N\)-heterocyclic carbene boroxine adduct by the reaction of 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (NHC) with 3-methylphenylboronic acid, which exhibits a carbene-facilitated condensation of the organic boronic acid.

**Experimental Section**

**General procedures**. All manipulations were carried out under a nitrogen atmosphere in an MB 150-GI glovebox or using standard Schlenk line techniques. All solvents were purified by standard methods before use. The NHC was prepared according to the literature procedure [20]. 3-Methylphenylboronic acid was purchased from Aldrich and was used as received. \(^1\text{H NMR spectra were recorded on a Bruker AM 400 spectrometer in dry deoxygenated CDCl}_3 as a solvent. Elemental analyses were performed on an Elemental Vario MICRO CUBE. Melting points were measured in sealed glass tubes.

**Synthesis of (3-MeC\(_6\)H\(_4\)_3B\(_3\)O\(_3\)(NHC) (1)**

To a solution of the NHC (0.152 g, 1.0 mmol) in toluene (10 mL) at 0 °C, a solution of 3-methylphenylboronic acid (0.340 g, 2.5 mmol) in toluene (20 mL) was added drop by drop via a syringe. The mixture was allowed to warm to room
temperature and stirred for 72 h. Then the solution was concentrated in vacuo to 3 mL, and hexane was added (5 mL). After filtration, the solution was stored and within 2 days I was obtained as colorless crystals. Yield: 0.308 g (73%). M. p. 147 – 149 °C. -1 HNMR (399.13 MHz, CDCl3, 25 °C, TMS): δ = 7.86 (s, 3H, Ar-H), 7.13 – 6.95 (m, 9H, Ar-H), 4.49 (q, 4H, -CH2), 2.41 (s, 6H, carbene-CH3), 2.21 (s, 3H, Ar(CH3)2-CH3), 2.07 (s, 6H, Ar(CH3)2-CH3). – C30H37B2N2O3 (506.06): calcd. C 71.20, H 3.73, N 5.53; found C 70.88, H 3.76, N 5.46%.

Crystal structure determination

Single crystals of I were selected from a Schlenk flask and protected by perfluorinated polyether oil. An appropriate crystal was mounted on a glass fiber. The intensity data for I were measured on a Rigaku AFC10 Saturn724 (2 × 2 bin mode) diffractometer with graphite-monochromatized MoKα (λ = 0.71073 Å) radiation. The structure was solved by Direct Methods (SHELXS-97) [21, 22] and refined by full-matrix least-squares methods on F2 using SHELXL-97 [21, 22]. All non-hydrogen atoms were located by difference Fourier syntheses and refined anisotropically. Hydrogen atoms were generated in idealized positions with Uiso related to the Ueq of the parent atoms. A summary of the crystal structure data is given in Table 1.

CCDC 916462 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The reaction of the N-heterocyclic carbene with 3-methylphenylboronic acid in a molar ratio of 1 : 3 resulted in the formation of the 1 : 1 adduct (3-MeC6H4)2B2O3(NHC) (I). The reaction proceeds under the elimination of 3 equiv. of water. Compound I is soluble in toluene, benzene, THF, and trichloromethane. It was characterized by 1H NMR spectroscopy in CDCl3 solution as well as by elemental analysis. The 1H NMR spectrum exhibits two sets of resonances for the Ar-Me groups in a ratio of 2 : 1, which indicates that the coordinated N-heterocyclic carbene is attached to one boron atom.

Single crystals of X-ray quality were obtained from a toluene-hexane solution of I at low temperature, crystallizing in the monoclinic space group P21/n with Z = 4 (Table 1). The structure determination unam-

Table 1. Crystallographic data for compound I.

| I | Formula C10H23B3N2O3 | M (g/mol) 506.05 | Crystal colour colorless | Crystal size, mm3 0.53 × 0.35 × 0.27 | Crystal system monoclinic | Space group P21/n | a, Å 13.698(4) | b, Å 14.410(4) | c, Å 14.947(4) | β, deg 103.006(4) | V, Å3 2874.5(15) | Z 4 | µ (MoKα), mm−1 0.1 | F(000), e 1080 | 2θ range, deg 2.08 – 29.13 | hkl range −18/14, −18/19, −18/20 | Refl. collected / independent 20380 / 7603 | Data / restraints / ref. params. 7603 / 17 / 412 | R1 / wR2 (I ≥ 2σ(I)) 0.0555 / 0.1291 | R1 / wR2 (all data) 0.1142 / 0.1605 | Goodness of fit (R2) 0.999 | Nρmax (max / min), e Å−3 0.132 / −0.203 |
Table 2. Bond lengths and NBO analysis of I and (3-MeC₆H₄)₂B₂O₃ from DFT calculations.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Compound I</th>
<th>Energy</th>
<th>Hybrid</th>
<th>Occupancy (%)</th>
<th>Energy</th>
<th>Hybrid</th>
<th>Occupancy (%)</th>
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<tr>
<td>B(1)–C(1)</td>
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<td>1.3533</td>
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<td>1.3833</td>
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<td>1.3553</td>
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<td></td>
<td>1.3833</td>
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<td>B(1)–N(1)</td>
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<td>1.3553</td>
<td></td>
<td></td>
<td>1.3833</td>
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<td></td>
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<tr>
<td>B(2)–C(2)</td>
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<tr>
<td>B(2)–N(2)</td>
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Scheme 1. Preparation of compound I.

In general, formation of (RBO)₃ from organic boronic acids RB(OH)₂ requires phosphorus pentoxide or sulfuric acid for the dehydration or prolonged heating in toluene [27]. In contrast to these methods, the condensation of RB(OH)₂ reported here is more facile and gives higher yields without heating or other auxiliaries. The boroxine ring-forming reaction is an entropically driven process due to the elimination of water. 3-Methylphenylboronic acid and [OB(3-MeC₆H₄)]₃ are forming an equilibrium in solution at room temperature. In the presence of the N-heterocyclic carbene, product I possesses a higher stability towards ring-opening compared to its parent compound [OB(3-MeC₆H₄)]₃ (Scheme 1). The geometry change of one boron atom from trigonal to tetrahedral on complexation with the N-heterocyclic carbene may be responsible for a relief of the ring strain in [OB(3-MeC₆H₄)]₃. However, further adduct formation of I with an excess of the N-heterocyclic carbene was not observed even at elevated temperatures. With catalytic amounts of NHC, we were not able to isolate compound I or the NHC-free boroxine. The trapping of a monomeric...
Table 3. Bond angles of product 1 and (3-MeC₆H₄)₂B₃O₃ from DFT calculations.

<table>
<thead>
<tr>
<th>Angle (deg)</th>
<th>Product 1</th>
<th>(3-MeC₆H₄)₂B₃O₃</th>
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<tbody>
<tr>
<td>N(1)–C(1)–B(1)</td>
<td>124.58</td>
<td>–</td>
</tr>
<tr>
<td>N(2)–C(1)–B(1)</td>
<td>129.74</td>
<td>–</td>
</tr>
<tr>
<td>C(1)–B(1)–O(3)</td>
<td>108.78</td>
<td>–</td>
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<tr>
<td>O(1)–B(1)–O(3)</td>
<td>111.40</td>
<td>118.48</td>
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<tr>
<td>B(1)–O(1)–B(2)</td>
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<td>121.53</td>
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<tr>
<td>B(2)–O(2)–B(3)</td>
<td>120.66</td>
<td>118.45</td>
</tr>
<tr>
<td>C(1)–B(1)–O(3)</td>
<td>120.14</td>
<td>121.57</td>
</tr>
<tr>
<td>N(2)–C(1)–B(1)</td>
<td>120.81</td>
<td>118.44</td>
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</table>

adduct NHC-(R–B)=O is a challenge for further investigations.

Ab initio calculations were carried out with the density functional theory (DFT) approach using Becke three-parameter Lee-Yang-Parr (B3LYP) [28, 29] hybrid density functional and Pople’s 6-311+g** basis set [30, 31] with GAUSSIAN 09 [32] on the single molecule of 1 as well as on (3-MeC₆H₄)₂B₃O₃. Geometry optimizations were followed by frequency analysis to assure that the obtained structures are of minimum energy. The natural bond order analysis (NBO 3) [33–35] was performed to clarify the bonding situation in the molecules. The calculated bond lengths and bond angles are shown in Tables 2 and 3. They agree well with the crystallographic data of product 1. The NBO analysis (Table 2) shows that in both 1 and (3-MeC₆H₄)₂B₃O₃ the atoms B(2) and B(3) form single bonds with the sp²-hybridized carbon atom. In product 1, B(1) is sp³-hybridized to form a single bond with C(1) (sp³) and sp²-hybridized to produce a single bond with C(4) of the aromatic ring (sp²). In product 1 C(1) exhibits strong bonds with N(1) and N(2). They provide lone pairs that strengthen the B–O and B–C bonds through donor-acceptor interactions. The addition of the NHC only slightly lowers the B–C(aryl) bond energies, whereas the B(1)–C(1) bond energy is slightly higher than those of the other B–C bonds (Table 2).

Summary

The synthesis and the structure analysis of compound 1 has shown that the N-heterocyclic carbene facilitates the condensation of m-tolylboronic acid. This reaction type provides a facile route for the synthesis of N-heterocyclic carbene-boroxine adducts from boronic acids, and adds a new utility to the rich N-heterocyclic carbene chemistry.

Acknowledgement

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