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

Dongxiang Zhang[a], Jie Li[a], Xiao Dong[a], Xing Zhou[a], Zhi Yang[a], and Herbert W. Roesky[b]

[a] School of Chemical Engineering and Environment, Beijing Institute of Technology, 100081 Beijing, P. R. China

[b] Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Reprint requests to Dr. Zhi Yang. E-mail: zhiyang@bit.edu.cn or Professor Herbert W. Roesky. Fax: (+49) 551-39-3373. hroesky@gwdg.de

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The adduct of $(3\text{-MeC}_6H_4)_3B_3O_3$ 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 $(3\text{-MeC}_6H_4)_3B_3O_3(\text{NHC})$ (**1**) has been characterized by ^{1}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 σ-donor properties but very weak π-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}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 Elementar Vario MICRO CUBE. Melting points were measured in sealed glass tubes.

Synthesis of $(3\text{-MeC}_6H_4)_3B_3O_3(\text{NHC})$ (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

Table 1. Crystallographic data for compound **1**.

	1
Formula	$C_{30}H_{37}B_3N_2O_3$
M_r	506.05
Crystal colour	colorless
Crystal size, mm^3	$0.53 \times 0.35 \times 0.27$
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	13.698(4)
b, Å	14.410(4)
c, Å	14.947(4)
β, deg	103.006(4)
V, Å^3	2874.5(15)
Z	4
D_{calcd}, g cm^{-3}	1.17
μ(MoK_α), mm^{-1}	0.1
F(000), e	1080
2 θ range, deg	2.08 – 29.13
hkl range	−18/14, −18/19, −18/20
Refl. collected / independent	20 380 / 7603
Data / restraints / ref. params.	7603 / 17 / 412
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0555 / 0.1291
$R1$ / $wR2$ (all data)	0.1142 / 0.1605
Goodness of fit (F^2)	0.999
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.132 / −0.203

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 **1** was obtained as colorless crystals. Yield: 0.308 g (73 %). M. p. 147 – 149 °C. – ^{1}HNMR (399.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.86$ (s, 3H, Ar-*H*), 7.13 – 6.95 (m, 9H, Ar-*H*), 4.49 (q, 4H, -CH_2-), 2.41 (s, 6H, carbene-CH_3), 2.21 (s, 3H, $Ar_{(B1)}$-CH_3), 2.07 (s, 6H, $Ar_{(B2,B3)}$-CH_3), 1.17 ppm (tr, 6H, -CH_2CH_3). – $C_{30}H_{37}B_3N_2O_3$ (506.06): calcd. C 71.20, H 7.37, N 5.53; found C 70.88, H 7.36, N 5.46 %.

Crystal structure determination

Single crystals of **1** 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 **1** were measured on a Rigaku AFC10 Saturn724+ (2 × 2 bin mode) diffractometer with graphite-monochromatized MoK_α ($\lambda = 0.71073$ Å) radiation. The structure was solved by Direct Methods (SHELXS-97) [21, 22] and refined by full-matrix least-squares methods on F^2 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 U_{iso} related to the U_{iso} 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.

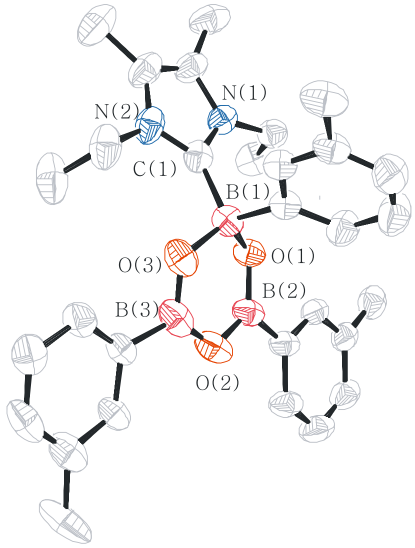


Fig. 1. Molecular structure of **1** in the crystal. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)–C(1) 1.651(3), B(1)–O(1) 1.478(2), B(1)–O(3) 1.480(2), C(1)–N(1) 1.349(2), C(1)–N(2) 1.356(2), B(2)–O(1) 1.346(2), B(2)–O(2) 1.393(2), B(3)–O(2) 1.393(3), B(3)–O(3) 1.334(3); N(1)–C(1)–B(1) 125.14(15), N(2)–C(1)–B(1) 129.66(15), C(1)–B(1)–O(3) 109.08(15), O(1)–B(1)–O(3) 110.34(14), B(1)–O(1)–B(2) 121.21(14), B(1)–O(3)–B(3) 122.19(16), O(1)–B(2)–O(2) 120.47(18), B(2)–O(2)–B(3) 118.98(15), O(3)–B(3)–O(2) 121.10(16).

Results and Discussion

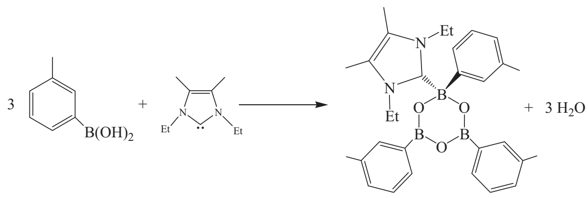
The reaction of the *N*-heterocyclic carbene with 3-methylphenylboronic acid in a molar ratio of 1 : 3 resulted in the formation of the 1 : 1 adduct (3-$MeC_6H_4)_3B_3O_3$(NHC) (**1**). The reaction proceeds under the elimination of 3 equiv. of water. Compound **1** is soluble in toluene, benzene, THF, and trichloromethane. It was characterized by ^{1}H NMR spectroscopy in $CDCl_3$ solution as well as by elemental analysis. The ^{1}H 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 **1** at low temperature, crystallizing in the monoclinic space group $P2_1/n$ with $Z = 4$ (Table 1). The structure determination unam-

Table 2. Bond lengths and NBO analysis of **1** and $(3\text{-}MeC_6H_4)_3B_3O_3$ from DFT calculations.

Distance	Compound **1**				$(3\text{-}MeC_6H_4)_3B_3O_3$			
	Å	Occupancy (%)	Hybrid	Energy	Å	Occupancy (%)	Hybrid	Energy
B(1)–O(1)	1.4807				1.3832			
B(1)–O(3)	1.4823				1.3835			
B(2)–O(1)	1.3525	16.93	B(2)$sp^{2.31}$, O(1)$sp^{0.25}$	−0.99702	1.3833	16	B(2)$sp^{2.69}$, O(1)$sp^{0.26}$	−1.03169
B(3)–O(3)	1.3533	16.85	B(3)$sp^{2.50}$, O(3)$sp^{0.25}$	−0.99766	1.3831	16	B(3)$sp^{2.38}$, O(3)$sp^{0.26}$	−1.03219
B(2)–O(2)	1.3892				1.3833			
B(3)–O(2)	1.3910	16.04	B(3)$sp^{2.67}$, O(2)$sp^{0.28}$	−0.98301	1.3837	16	B(3)$sp^{2.69}$, O(2)$sp^{0.26}$	−1.03169
B(1)–C(1)	1.6815	29.31	B(1)$sp^{3.03}$, C(1)$sp^{1.18}$	−0.51114			–	
B(1)–C(4)	1.6329	32.36	B(1)$sp^{2.71}$, C(4)$sp^{1.90}$	−0.46459	1.5516	32.94	B(1)$sp^{1.73}$, C(4)$sp^{2.03}$	−0.53401
B(2)–C(2)	1.5701	32.15	B(2)$sp^{1.49}$, C(2)$sp^{2.21}$	−0.49682	1.5514	32.68	B(2)$sp^{1.18}$, C(2)$sp^{2.04}$	−0.53607
B(3)–C(3)	1.5711	32.03	B(3)$sp^{1.26}$, C(3)$sp^{2.01}$	−0.49902	1.5516	32.79	B(3)$sp^{1.42}$, C(3)$sp^{2.04}$	−0.53536
C(1)–N(1)	1.3543	35.76	C(1)$sp^{2.73}$, N(1)$sp^{1.85}$	−0.83917			–	
		25.42	C(1)p, N(1)p	−0.35764			–	
C(1)–N(2)	1.3555	35.83	C(1)$sp^{2.64}$, N(2)$sp^{1.84}$	−0.84269			–	

biguously ascertains the composition of **1**. Its molecular structure, as shown in Fig. 1, contains three tolyl rings, each bound to one of the three boron atoms of a six-membered B_3O_3 ring. In addition, the five-membered *N*-heterocyclic carbene is coordinated to one of three boron atoms B(1) through a Lewis acid-base interaction. B(1) exhibits a tetrahedral environment with angles of 109.08(15)–129.66(15)°. The other two boron atoms are three-coordinate, and the oxygen atoms are two-coordinate. The bond angles between the annular atoms are in the range of 118.98(15) to 121.10(16)°. The B–O bond lengths at B(1) of 1.479(2) Å (av) are considerably longer than the remaining B–O distances, which is due to the increased coordination number at B(1) from three to four (Fig. 1). A similar situation was observed in a previously reported boroxine Lewis base adduct [23]. The B–O(2) bond length is significantly longer (1.393(2) Å av) when compared with those of B(2)–O(1) and B(3)–O(3) (1.340(2) Å av), which might be due to the increased polarity of the latter. A parallel tendency of the B–O bond lengths was observed in the structure of $(4\text{-}MeC_6H_4)_3B_3O_3{\cdot}NH_2C_6H_{11}$ [24]. The sum of the internal angles of the B_3O_3 ring is 714.29° indicating a non-planar ring system (sum 720°). In contrast, in the structure of $(PhBO)_3$·pyridine, the B_3O_3 ring is nearly planar with a sum of the angles of 719.0° [25]. This shows that the conformation at theB(1) atom in **1** is more distorted when compared with that of $(PhBO)_3$·pyridine. This might be due to the bulk of the *N*-heterocyclic carbene or its stronger Lewis base character. The B–$C_{(carbene)}$ bond length of **1** is 1.651(3) Å which is shorter when compared with that of NHC·BF_3 [26].



1

Scheme 1. Preparation of compound **1**.

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 $[OB(3\text{-}MeC_6H_4)]_3$ are forming an equilibrium in solution at room temperature. In the presence of the *N*-heterocyclic carbene, product **1** possesses a higher stability towards ring-opening compared to its parent compound $[OB(3\text{-}MeC_6H_4)]_3$ (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 $[OB(3\text{-}MeC_6H_4)]_3$. However, further adduct formation of **1** 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 **1** or the NHC-free boroxine. The trapping of a monomeric

Table 3. Bond angles of product **1** and $(3\text{-}MeC_6H_4)_3B_3O_3$ from DFT calculations.

Angle (deg)	**1**	$(3\text{-}MeC_6H_4)_3B_3O_3$
N(1)–C(1)–B(1)	124.58	–
N(2)–C(1)–B(1)	129.74	–
C(1)–B(1)–O(3)	108.78	–
O(1)–B(1)–O(3)	111.40	118.48
B(1)–O(1)–B(2)	123.43	121.53
B(1)–O(3)–B(3)	123.16	121.53
O(1)–B(2)–O(2)	120.66	118.45
B(2)–O(2)–B(3)	120.14	121.57
O(3)–B(3)–O(2)	120.81	118.44

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 $(3\text{-}MeC_6H_4)_3B_3O_3$. 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 $(3\text{-}MeC_6H_4)_3B_3O_3$ the atoms B(2) and B(3) form single bonds with the sp^2-hybridized carbon atom. In product **1**, B(1) is $sp^{3.03}$-hybridized to form a single bond with C(1) ($sp^{1.18}$) and $sp^{2.71}$-hybridized to produce a single bond with C(4) of the aromatic ring ($sp^{1.90}$). 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.

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