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Boron bis-(4-methylbenzoxazol-2-yl)-methanide complexes†

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Boron compounds have attracted the attention of chemists because of their unique catalytic properties and potential wider material applications. Although group 13 metal compounds, which are based on the bis-(benzoxazol-2-yl)-methane system (Box, ({NCOC $_6$ H $_4$ } $_2$ CH $_2$)), have been reported in the last several years, boron containing Box compounds were still missing. Now we report their successful syntheses and spectroscopic characterisation in this work. The borane compound [({NCOC $_6$ H $_3$ } $_2$ CH)BH $_2$] (1) and haloboranes [({NCOC $_6$ H $_3$ } $_2$ CH)BF $_2$] (2), [({NCOC $_6$ H $_3$ } $_2$ CH)BCl $_2$] (3) and [({NCOC $_6$ H $_3$ } $_2$ CH)BBr $_2$] (4) were characterised in the solid state by single crystal X-ray diffraction and in solution by NMR techniques. In addition, the fluorescence properties of compounds 1–4 are communicated.

Introduction

Within the domains of coordination and organometallic chemistry, the landscape has been significantly shaped by the prominence of stable chelates arising from N,N-bidentate monoanionic ligands. These chelates stand as enduring subjects of exploration, revealing a myriad of captivating structural, chemical, and physical attributes exhibited by their associated metal complexes.² In recent decades, the compelling idea of replacing established, rare, and expensive metals in catalysis has driven continuous efforts to explore reactions mediated by cheaper main-group elements.3 Boron, a metalloid, exhibits distinct catalytic properties and potential owing to its straddling of metals and nonmetals. This is particularly evident when coupled with welldesigned ligands or strong electron donors (NHCs, CAACs etc.), for example, σ bond activations (H-H, C-H or C-F etc.) and/or FLP (frustrated Lewis pair) as catalysts. Impressively, N,N'-chelated boron difluoride dipyrromethene (F-BODIPY), has proved to be an outstanding fluorescent dye, leveraging its exceptional chemical stability and high fluorescence quantum efficiency.^{5,6}

Since 2014, our group successfully synthesised and characterized several N,N'-chelated metal bisheterocyclomethanide compounds. Alkali metal compounds⁷ such as $[BoxLi(OEt_2)_2]$, $[\{Na(THF)_6\}\{(^{4-Me}Box)_2Na\}]$, $[(^{4-Bzh}BoxM)_2]^{10}$ (M = K, Rb, Cs), alkaline earth metal compounds such as $[(^{2,4-iPr}BoxM)_2]^{11}$ (M = Mg, Ca, Sr, Ba) and group 13 element compounds such as

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[$\{^{4\text{-Me}}\text{BoxAlH}\}$ - $\{\text{HAl}^{\text{Dipp}}\text{BDI}\}$] 12 (Dipp = 2,6-diisopropylphenyl, BDI = β -diketiminate), [$^{4\text{-Bzh}}\text{BoxM}$] 13 (M = AlX₂, Ga, In, Tl, where X = H, Me, I) were published. Taking these considerations into account, we are introducing a class of boron compounds chelated by the Box ligand to extend the work to the yet missing group 13 element.

Results and discussion

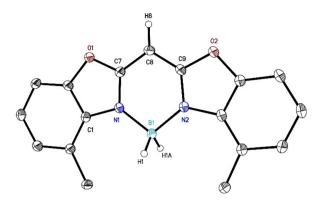
Synthesis and characterisation of compounds 1-4

The discussed bisheterocyclomethanide ligand ([$\{4-\text{MeNCOC}_6H_3\}_2\text{CH}$], in the following $^{4-\text{Me}}\text{Box}$) was prepared by our group before. ¹⁴ The deprotonation of the methane ligand starts by treating it with the commercially available borane tetrahydrofuran complex solution in THF or toluene at 95 °C for 2 days. The volatiles were removed under reduced pressure and the clear solution was cooled to -30 °C for 24 hours to obtain the formed yellow crystals of 1 in varying yields (36%–45%) (Scheme 1).

SC-XRD experiments revealed the crystal structure of 1 unambiguously to be monomeric, as depicted in Fig. 1. 1 crys-

Scheme 1 Synthesis of [($\{4-MeNCOC_6H_3\}_2CH\}BH_2$] (1) by deprotonation with BH_3 ·THF solution in THF or toluene.

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structure of [({4-MeNCOC₆H₃}₂CH)BH₂] Anisotropic displacement parameters are depicted at the 50% probability level. Two hydrogen atoms (H1, H1A) were refined freely. All ligand based hydrogen atoms are omitted for clarity except H8.

tallises in the orthorhombic space group Pnma with half a molecule in the asymmetric unit on the crystallographic mirror plane. The molecule consists of a boron atom, which is κ²-N,N-chelated by two nitrogen atoms of the NacNac-akin moiety from the 4-Me Box ligand.

The N,N-bite angle of compound 1 N(1)-B(1)-N(2) is 104.71 (10)°, while the H(1)-B(1)-H(1A) angle is 111.3(12)°, which is close to the ideal tetrahedral angle. The B-N bond lengths (d(B1-N1) = 1.5770(18) Å, d(B1-N2) = 1.5824(18) Å) are slightly longer than those in BODIIM (boron diimidazolylmethene) (1.546(1) and 1.550(1)) that were published before. 15 The C₃N₂ unit in [4-MeBox-BH2] (1) shows bond lengths of 1.3883(2) Å (C7-C8) and 1.3901(19) Å (C8-C9) and of 1.3373(2) Å (N1-C7)

Scheme 2 Synthesis route of compounds 2-4.

and 1.3381(2) Å (N2-C9). Interestingly, the planar molecule reveals crystallographic m symmetry and thus, neither a dislocation of the boron atom from the C₃N₂ moiety nor a butterfly folding between both benzoxazyl moieties is observed as in many other bis-(benzoxazol-2-yl)-methanide complexes.

The first attempts to prepare boron dihalide compounds with a metathesis reaction of the respective lithium [4-MeBoxLi $(OEt_2)_2$ ¹⁶ or potassium compound [^{4-Me}BoxK]¹⁷ with boron trihalides failed. Herein, we synthesised 4-MeBox supported boron dihalide compounds 2-4 from compound 1 and boron trihalides in excellent yields of 90%-95% (Scheme 2).

All compounds 2-4 are prepared through the same treatment of 1 with 5.0 eq. of the corresponding boron trihalides in toluene at 95 °C. After 3 days, the solvent was removed under reduced pressure and the crude products were washed with cold *n*-pentane several times. The pure compounds 2-4 could be obtained after drying the products in vacuo. These three products have poor solubility in most aromatic solvents, which poses a great challenge to crystallisation. This work finally used different methods to crystallise the three products (see Experimental). The molecular structures of [4-MeBoxBF₂] (2), $[^{4-Me}BoxBCl_2]$ (3) and $[^{4-Me}BoxBBr_2]$ (4) are depicted in Fig. 2.

2 crystallises in the orthorhombic space group Pnma with half a molecule in the asymmetric unit. 3 and 4 crystallise in the monoclinic space groups $P2_1/m$ and $P2_1$, respectively; 3 with half a molecule and 4 with one molecule in the asymmetric unit. It is worth mentioning that 2 and 3 show crystallographic m symmetry as well and therefore display no dislocation of the boron atom from the C₃N₂ plane. No folding angle can be observed either, like for compounds 1 and 2. However, 4 shows only non-crystallographic m symmetry and therefore a slight folding of 2.63(4)°. Structural data are listed in Table 1.

The successful synthesis of compounds 1-4 is further substantiated by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (LIFDI) and elemental analysis (see the ESI†). The ¹H NMR spectrum of 1 shows a singlet resonance at 5.01 ppm (H8) while the signal observed in the ¹¹B NMR spectrum at -5.46 appears very broad without a visible B-H coupling. In contrast to that, the 11B NMR spectrum of 2 shows a very sharp triplet as a result of the coupling to the two fluorine atoms with ${}^{1}J_{^{11}B-F} = -27$ Hz (the sign of the one-bond B-F

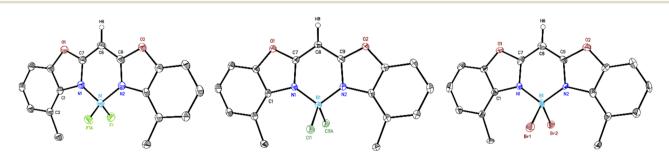


Fig. 2 Molecular structures of [((4-MeNCOC₆H₃)₂CH)BF₂] (2, left), [((4-MeNCOC₆H₃)₂CH)BCl₂] (3, middle) and [((4-MeNCOC₆H₃)₂CH)BBF₂] (4, right). Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms have been omitted for clarity, except H8.

Table 1 Selected bond lengths [Å] and angles [°] for compounds 1–4 (X = H. F. Cl. Br)

	1 (X = H)	2(X = F)	3(X = Cl)	4 (X = Br)
B(1)-N	1.5770(18)	1.558(2)	1.542(2)	1.537(9)
. ,	1.5824(18)	1.569(2)	1.542(2)	1.538(8)
B(1)-X	1.118(13)	1.3853(13)	1.8692(11)	2.046(7)
. ,	()	,	()	2.028(6)
C(7)-C(8)	1.3883(18)	1.388(2)	1.377(2)	1.365(9)
C(8)-C(9)	1.3901(19)	1.384(3)	1.382(2)	1.362(9)
C(7)-N(1)	1.3373(17)	1.341(2)	1.349(2)	1.356(8)
C(9)-N(2)	1.3381(17)	1.346(2)	1.349(2)	1.363(8)
N-B(1)-N	104.71(10)	106.01(13)	108.37(13)	109.5(4)
$B(1)\cdots C_3N_2$	0	0	0	0.026(9)
Folding angle	0	0	0	2.63(4)

coupling is known to be negative in most cases¹⁸). The corresponding ¹⁹F signal consists of a 1:1:1:1 quartet due to the coupling to the spin 3/2 nucleus ¹¹B, with ¹⁰B satellites visible $\binom{1}{J_{10B-F}} = -9$ Hz), which are shifted towards higher frequencies due to the isotope shift. In addition to that, the ¹H and ¹³C signals of the ligand's methyl groups show a small triplet splitting that vanishes upon 19F decoupling and thus indicates a through-space interaction between the methyl groups and the close-by fluorine atoms ($d_{H-F} \approx 2.3 \text{ Å}, J_{H-F} = 1.9 \text{ Hz}, d_{C-F} \approx 3 \text{ Å},$ J_{C-F} = 7 Hz). Both 3 and 4 show very similar ¹H NMR spectra compared to 2 with the chemical shift of the H8 proton experiencing a slight upfield shift with increasing weight of the coordinating halogen atoms (5.08 ppm for 2, 4.93 ppm for 3 and 4.90 ppm for 4), while, in particular, compound 4 suffers from very low solubility in both toluene- d_8 and THF- d_8 . The ¹¹B signals of 3 and 4 are only slightly broader than that of 2 without any visible coupling to the heavier halogens chlorine and bromine due to quadrupolar relaxation of the Cl/Br isotopes.

The IR spectrum of compound 1 displays a B-H stretching band at $\nu = 2353 \text{ cm}^{-1}$, which is very close to the calculated value of $\nu = 2435$, 2494 cm⁻¹ at the B3LYP/Def2TZVP level of theory and significantly higher than that in bis(phosphinimino)amide borondihydride reported by Singh *et al.* ($\nu = 2096$, 2057 cm⁻¹).²⁶

The UV emission spectrum of compound 1 was recorded with $c = 10^{-4}$ mol L⁻¹ in THF. As shown in Fig. 3, the emission maximum of 1 is λ_{ex} = 452 nm. The quantum yield amounts to 75.5%, with a subsequent reduction to 59.2% following an 18-hour exposure of the solution to ambient air. The emission spectra of compounds 2-4 were recorded at the same concentration but in toluene (Fig. 3). It can be concluded from the normalized emission spectrum that all three compounds emit at a similar wavelength. A slight redshift can be observed from 2 to 4, with the highest emission shifting from 388 nm (2) to 396 nm (3) and eventually 404 nm (4), respectively. The emission peaks of BODIPY compounds are mostly found around or higher than 500 nm. Hence, the compounds we introduced in this work have significantly lower emission maxima than BODIPY. They are pure blue fluorescence emitting materials in any feasible application.

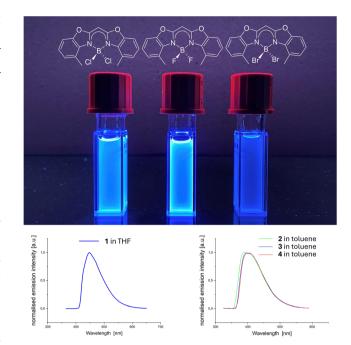


Fig. 3 Top: $[^{4-Me}BoxBF_2]$ (2, mid), $[^{4-Me}BoxBCl_2]$ (3, left) and $[^{4-Me}BoxBBr_2]$ (4, right) at the same concentration (10^{-4} M) under UV-light; bottom left: normalised emission spectrum of 1 in THF; bottom right: normalized emission spectra of 2–4 in toluene (all at $c=10^{-4}$ M).

Conclusions

To conclude, the desired bis-(benzoxazol-2-yl)methanide ligand (4-MeBox) based borane compound [4-MeBoxBH₂] (1) and haloborane compounds [4-MeBoxBF₂] (2), [4-MeBoxBCl₂] (3) and [4-MeBoxBBr₂] (4) have successfully been synthesised and the portfolio of group 13 complexes has been completed. All obtained products were analysed by NMR spectroscopy, elemental analysis, mass spectrometry (LIFDI), single crystal XRD experiments and fluorescence measurements. The desired bisheterocyclomethanide ligated haloborane compounds most probably combine the best of two worlds: the stabilization abilities for future low-oxidation boron compounds and the high-performance fluorescence in materials. This and the possible small molecule activations of low-oxidation state boron based on compounds 1-4 are currently under investigation.

Experimental

General procedures

All air and moisture sensitive reactions were carried out using Schlenk techniques under an argon atmosphere, and the products were stored in an argon glovebox. The used solvents were distilled from Na or K and stored under argon over 3 Å molecular sieves before use. The discussed ligand [$\{4-MeNCOC_6H_3\}_2CH_2$] was synthesised according to literature procedures. The starting materials were purchased commer-

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cially. The 1H, 11B, 13C, and 19F NMR spectroscopic data were recorded on a Bruker Avance III 300 MHz, a Bruker Avance III 400 MHz and a Bruker Avance III 500 MHz instrument and referenced to the respective deuterated solvent. LIFDI-MS spectra were recorded on a Jeol AccuTOF spectrometer. Elemental analyses for the determination of the mass fraction of C, H, and N were carried out on an Elementar Vario EL3 at the Institute of Inorganic Chemistry, University of Göttingen. IR spectra were recorded inside a glovebox on an Agilent Technologies Cary 640 FTIR spectrometer equipped with a ZnSe module and analysed using FTIR MicroLab software. Fluorescence analyses were conducted using a FluoroMax-4 spectrometer from HORIBA Jobin Yvon. The quantum yield was determined with the quanta-φ integrating sphere. At the host computer, the software FluorEssence v3.0 and OriginPro 8.5G were used to record the information of the fluorescence spectra and analyze the data in the graph. The single crystals were selected under cold protective conditions with the X-Temp2 device. 19 The diffraction data were collected using an Incoatec Mo Microsource and a Bruker APEX II detector on a D8 goniometer. The data were integrated with SAINT.²⁰ A multi-scan absorption correction was applied using SADABS²¹ or TWINABS.²² The structures were solved by SHELXT²³ and refined on F² using SHELXL²⁴ in the graphical user interface ShelXle. 25 CCDC 2333148-2333151.†

[4-MeBoxBH₂] (1). Bis-(4-methylbenzoxazol-2-yl)-methane (400 mg, 1.44 ml, 1.00 eq.) and the borane tetrahydrofuran complex solution (2.87 mmol, 1.00 M, 2.87 ml, 2.00 eq.) were dissolved in 20 ml toluene or THF and heated at 85 °C for 48 hours. Crystals suitable for SC-XRD experiments were obtained from a saturated toluene solution at −30 °C overnight (yield: 36%–45%). NMR: ¹H (400 MHz, 298 K, THF-d₈, ppm): 7.05-6.99 (m, 6H, Ar-H), 5.01 (s, 1H, H8), 2.77(s, 6H, H16). ¹H (400 MHz, 298 K, tol-d₈): 6.75-6.62 (m, 6H, Ar-H), 4.72 (s, 1H, H8), 2.76 (s, 6H, H16). Note: Compound 1 has poor solubility in toluene and almost all aromatic solvents. $^{13}\text{C}\{^1\text{H}\}\ (101 \text{ MHz}, 298 \text{ K}, \text{THF-}d_8): 166.08 \text{ (s, 2C, C7)},$ 149.84 (s, 2C, C6), 133.88 (s, 2C, C1), 125.62 (s, 2C, C4), 123.55 (s, 2C, C3), 108.16 (s, 2C, C5), 56.05 (s, 1C, C8), 18.10 (s, 2C, C16). ¹¹B (96 MHz, 298 K, THF- d_8): -5.46 (s); ¹¹B{¹H} (96 MHz, 298 K, THF-d₈): -6.03 (s). Elemental analysis: C₁₇H₁₅BN₂O₂, calculated C 70.38, H 5.21, N 9.66; observed C 69.84, H 5.25, N 9.75. LIFDI-MS: calculated exact mass: 290.12 m/z; observed m/z: 290.1[M]⁺, 278.1 [M - BH]⁺.

[$^{4\text{-Me}}$ BoxBF₂] (2). [$^{4\text{-Me}}$ BoxBH₂] (1) (62 mg, 0.214 mmol, 1.00 eq.) and boron trifluoride etherate (0.28 mL, 48%, 1.12 g mL⁻¹, 1.07 mmol, 5.00 eq.) were dissolved in toluene (15 mL) in a Schlenk flask under an argon atmosphere while stirring. The flask was heated with an oil bath to 95 °C for 3 days. The solution turned yellow and some solid material precipitated. The solvent was removed under reduced pressure, the solid was washed with cold *n*-pentane several times, and then the product was dried in a vacuum. (Yield: 90%-95%, depending on washing.) Crystals suitable for SC-XRD experiments were obtained in a saturated acetone solution. NMR: ¹H (300 MHz, 298 K, tol-d₈, ppm): 6.81-6.70 (m, 6H, Ar-H), 5.08 (s, 1H, H8),

2.85 (s, 6H, H16). Note: Compound 2 has poor solubility in toluene and almost all aromatic solvents. ¹³C{¹H} (75 MHz, 298 K, tol-d₈): 125.97 (s, 2C, C4), 123.65 (s, 2C, C3), 107.16 (s, 2C, C5), 58.05 (s, 1C, C8), 18.92 (s, 2C, C16). ¹¹B (96 MHz, 298 K, tol- d_8): 2.30 (t, J = -27.1 Hz). ¹⁹F (282 MHz, 298 K, tol d_8): -115.96 (q, $J_{B-F}^{11} = -27.0$ Hz). ¹⁹F (377 MHz, 298 K, THF d_8): -117.13 (q, $J^{11}_{B-F} = -27.0$ Hz). Elemental analysis: C₁₇H₁₃BF₂N₂O₂, calculated C 62.61, H 4.22, N 8.59; observed C 61.49, H 4.22, N 9.08. **LIFDI-MS** m/z: 328.9 $[(2M + 4H)/2]^{+}$ (possible dimer).

[4-MeBoxBCl₂] (3). The synthesis of [4-MeBoxBCl₂] (3) was performed using a similar procedure to that employed for the preparation of 2, but by using boron trichloride solution (1.00 M in toluene, 5.00 eq.) instead. The solvent was removed under reduced pressure and washed with n-pentane several times, and then the product was dried in a vacuum. (Yield: 90-95%, depending on washing.) Crystals suitable for SC-XRD experiments were obtained in a saturated toluene solution. **NMR**: 1 H (300 MHz, 298 K, tol- d_{8} , ppm): 6.84–6.68 (m, 6H, Ar– H), 4.93 (s, 1H, H8), 3.18 (s, 6H, H16). Note: Compound 3 has poor solubility in toluene and almost all aromatic solvents. ¹³C ¹H} Because of the poor solubility, the spectra cannot be effectively observed. ^{11}B (96 MHz, 298 K, tol- d_8): 4.71 (s). ^{11}B (193 MHz, 298 K, THF- d_8): 4.47 (s). Elemental analysis: C₁₇H₁₃BCl₂N₂O₂, calculated C 56.87, H 3.65, N 7.80; observed C 55.30, H 3.65, N 8.40. **LIFDI-MS** m/z: 360.2 [M + H]⁺.

 $[^{4-Me}BoxBBr_2]$ (4). The synthesis of $[^{4-Me}BoxBBr_2]$ (4) was performed using a similar procedure to that employed for the preparation of 2, but by using boron tribromide solution (1.00 M, 5.00 eq.). The solvent was removed under reduced pressure and washed with n-pentane several times, and then the product was dried in a vacuum. (Yield: 90-95%, depending on washing.) Crystals suitable for SC-XRD experiments were obtained in a saturated toluene solution by slowly cooling an oil bath from 150 °C to room temperature. NMR: ¹H (300 MHz, 298 K, tol-d₈, ppm): 6.85–6.67 (m, 6H, Ar-H), 4.90 (s, 1H, H8), 3.35 (s, 6H, H16). Note: Compound 4 has extremely poor solubility in toluene, THF, and in almost all solvents. 11B (128 MHz, 298 K, THF- d_8): -3.85 (s). Elemental analysis: C₁₇H₁₃BBr₂N₂O₂, calculated C 45.95, H 2.93, N 6.25; observed C 39.50, H 2.40, N 6.25. **LIFDI-MS** m/z: 449.0 [M + H]⁺.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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