

COMMUNICATION

Intramolecular N-coordination in ketiminoboranes

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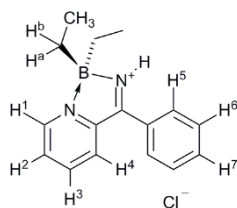
Electronic Supplementary Information:

Experimental

General considerations

All experiments were performed under a nitrogen atmosphere unless stated otherwise. Dry solvents were distilled off sodium (THF, toluene, diethyl ether, hexane) or CaH₂ (acetonitrile, dichloromethane) for the preparation of **4a**·HCl and **4c**·HCl or from a solvent purification system (**4b**·BF₃). All chemicals were commercially available and used as received. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer or a Bruker Avance III 500 MHz spectrometer. ¹¹B NMR spectra were referenced to BF₃·Et₂O and ¹⁹F NMR spectra referenced to CFCl₃. Electron impact (EI) mass spectra were obtained using a KRATOS MS890 double focussing magnetic sector instrument; electrospray (ESI) spectra were recorded on a KRATOS Concept or Quattro LC mass spectrometer. Elemental analyses were carried out on an Exeter CE-440 Elemental Analyser.

Syntheses

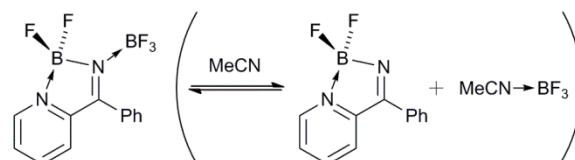


Preparation of **4a**·HCl·THF

A solution of Li[N(SiMe₃)₂] (0.452 g, 2.73 mmol) and 2-benzoylpyridine (0.500 g, 2.73 mmol) in PhMe (20 mL) was heated to 90 °C for 18 h. The solvent was removed *in vacuo* and the red residue redissolved in THF (25 mL). Me₃SiCl (0.35 mL, 2.75 mmol) was added and the reaction mixture heated to 45 °C for 2 h. The reaction mixture was cooled to -78 °C, Et₃BOMe (2.73 mL, 1.0 M in THF, 2.73 mmol) was added dropwise and the reaction allowed to slowly warm to room temperature. Colourless blocks grew from the solution over 3 d, isolated by filtration, washed with THF (2 × 10 mL) and dried *in vacuo* to give **4a**·HCl·THF as white hygroscopic crystals. Yield: 0.350 g, 37%.

¹H NMR (500 MHz, CDCl₃, ppm) δ_H = 16.3 (1H, br s, NH), 9.77 (1H, d, J = 5.5 Hz, H^a), 8.70 (1H, t, J = 7.9 Hz, H^b), 8.58 (1H, d, J = 8.1 Hz, H^c), 8.28 (1H, t, J = 6.6 Hz, H^d), 8.16 (2H, d, J = 7.3 Hz, 2×H^e), 7.68 (1H, tt, J = 7.4,

1.5 Hz, H^f), 7.61 (2H, t, J = 7.9 Hz, 2×H^g), 1.07 (2H, dq, J = 15.3, 7.7 Hz, 2×BCH^aH^bCH₃), 0.79 (2H, dq, J = 15.3, 7.7 Hz, 2×BCH^aH^bCH₃), 0.49 (6H, t, J = 7.7 Hz, 2×BCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm) δ_C = 165.40, 146.24, 143.28, 142.88, 134.21, 130.08, 129.72, 128.90, 126.49, 126.35, 14.45, 8.54. ¹¹B{¹H} NMR (100 MHz, CDCl₃, ppm) δ_B = 8 (s). **Elemental analysis** found C 62.4, H 7.1, N 9.0%. Calc. for C₁₅H₁₈N₃B·HCl·1.15H₂O C 62.5, H 7.3, N 9.1%. **MS (ESI+)** m/z = 250.17 (23%), 251.17 (100%), 252.17 (18%) [M+H]⁺



Preparation of **4b**·BF₃

A solution of Li[N(SiMe₃)₂] (0.837 g, 5.00 mmol) and 2-benzoylpyridine (0.916 g, 5.00 mmol) were heated in PhMe (40 mL) at 90 °C for 18 h to afford a dark red solution. The solvent was removed *in vacuo* and the red residue redissolved in THF (50 mL). Me₃SiCl (0.543 g, 5.00 mmol) was added and the reaction mixture heated to 45 °C for 2 h to afford a yellow-orange solution. The reaction mixture was cooled to -78 °C, BF₃·Et₂O (1.23 mL, 10 mmol) was added dropwise and the reaction allowed to slowly warm to room temperature. Colourless blocks formed on standing for 3 d which were isolated by filtration and dried *in vacuo* to give **4b**·BF₃ as white crystals. Yield: 0.910 g, 3.06 mmol, 61%.

¹¹B and ¹⁹F NMR data are consistent with the presence of an equilibrium between **4b**·BF₃ and **4b** and BF₃·MeCN in solution. NMR are shown below for this system (Fig. ESI-1). Both the ¹H and ¹³C NMR spectra are significantly complicated by the presence of a mixture of these two different components in solution, resulting in multiple overlapping signals which were not assigned.

¹¹B{¹H} NMR (160 MHz, CD₃CN, ppm) δ_B = 8 (t, BF₂, ¹J_{BF} = 25.4 Hz), 6 (t, BF₂, ¹J_{BF} = 22.8 Hz), 1 (q, BF₃, ¹J_{BF} = 14.5 Hz), 0 (s, BF₃·MeCN). ¹⁹F NMR (471 MHz, CD₃CN, ppm) δ_F = -141.5 (q, BF₃, ¹J_{BF} = 14.5 Hz), -151.9 (s, BF₃), -159.5 (q, BF₂, 25.0 Hz), -159.2 (q, BF₂, 22.5 Hz). **Elemental analysis** found C 48.2, H 3.8, N 8.5%. Calc. for C₁₂H₉N₃B₂F₅ C 48.4, H 3.0, N 9.4%.

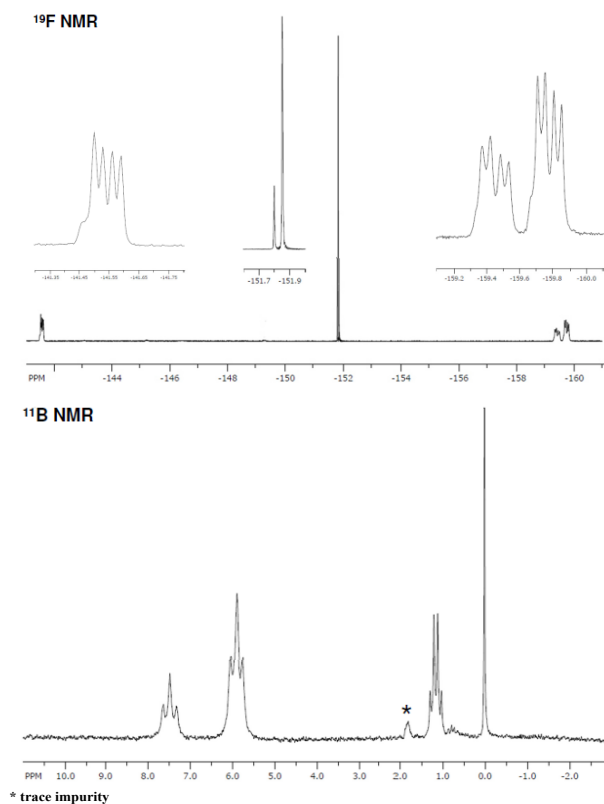
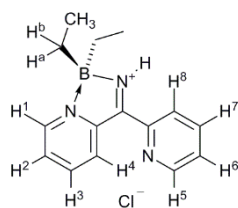


Fig. ESI-1 ^{19}F NMR (top) and ^{11}B NMR (bottom) of **4b**-BF₃ in MeCN



Preparation of **4c**-HCl·THF

A solution of lithium *bis*(trimethylsilyl)amide (0.426 g, 2.55 mmol) and 2,2'-dipyridyl ketone (0.500 g, 2.55 mmol) in PhMe (20 mL) and heated to 90 °C for 18 h. The solvent was removed *in vacuo* and the red residue redissolved in THF (20 mL). Me₃SiCl (0.33 mL, 2.6 mmol) was added and the reaction mixture heated to 40 °C for 2 h. The reaction mixture was cooled to -78 °C and Et₃BOMe (2.55 mL, 1.0 M in THF, 2.55 mmol) was added dropwise. The reaction was allowed to slowly warm to room temperature to give a pale brown precipitate under a dark brown liquid. The reaction mixture was filtered and colourless crystals grew from the filtrate over a period of 3 d. Yield: 0.252 g, 27%.

^1H NMR (500 MHz, CDCl₃, ppm) δ_{H} = 16.3 (1H, br s, NH), 9.77 (1H, d, J = 8.2 Hz, H^a), 9.69 (1H, d, J = 8.0 Hz, H^b), 8.84 (1H, dm, J = 4.3 Hz, H^c), 8.69 (1H, d, J = 5.6 Hz, H^d), 8.49 (1H, td, J = 7.7, 1.38 Hz, H^e), 8.10 (2H, m, H^f & H^g), 7.63 (1H, ddd, J = 7.7, 4.8, 1.0 Hz, H^h), 1.20 (2H, dq, J = 15.3, 7.7 Hz, BCH^aH^bCH₃), 0.88 (2H, dq, J = 15.3, 7.7 Hz, BCH^aH^bCH₃), 0.54 (6H, t, J = 7.7 Hz, BCH₂CH₃). $^{11}\text{B}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃, CDCl₃, ppm) δ_{B} = 8 (s). **Elemental analysis** (%): Found C 63.4, H 7.6, N 11.9%. Calc. for C₁₅H₁₈BN₃·HCl·0.9C₄H₈O C 63.4, H 7.5, N 11.9%.

Crystallography

Single crystals of **4a**-HCl·THF and **4c**-HCl·THF were mounted on glass fibres using fluoropolymer and examined on a Nonius Kappa CCD diffractometer using Mo-K α radiation (graphite monochromator, λ = 0.71073 Å). Temperatures were maintained using an Oxford Cryostream cooler. For compound **4a**-HCl·THF the crystals underwent a phase transition upon cooling to 180 K and data were collected at 240(2) K whereas **4c**-HCl·THF was collected at 180(2) K. Data collections were made using ω and ϕ scans using COLLECT.¹ Cells were indexed using HKL Scalepack and reduced using HKL, Denzo and Scalepack.² Data were corrected for absorption using symmetry equivalent reflections using the method of Blessing.³ A crystal of **4b**-BF₃ was mounted in paratone oil in a cryoloop and examined on a Bruker APEX CCD detector using Mo-K α radiation at 173(2) K with temperatures maintained using an Oxford Cryostream cooler. Data were collected using SMART software,⁴ reduced using SAINT,⁵ and an absorption correction applied using SADABS.⁶ Structures were solved using SHELXS-97 and refined using full matrix least squares methods on F^2 using SHELXL-97.⁷ The structure of **4c**-HCl·THF crystallised in the acentric space group P2₁. Although the Flack parameter indicated possible merohedral twinning, there are two molecules in the asymmetric unit related via a non-crystallographic inversion centre (the molecules differ primarily in the orientation of the pyridyl groups on the cyclic backbone, Fig. ESI-2). Thus the crystal inherently comprises an equal mixture of both left- and right-handed isomers. Since the final R values were acceptable and the refinement clearly reveals that the structure containing both 'hands' in a 1:1 ratio no attempt was made to resolve the twin since determination of the absolute structure is of limited chemical meaning. Figures for publication were prepared using Mercury version 3.3.⁸ A summary of crystallographic data is presented in Table ESI-1 and the final structures available in crystallographic cif format. CCDC deposit numbers 1043411-1043413.

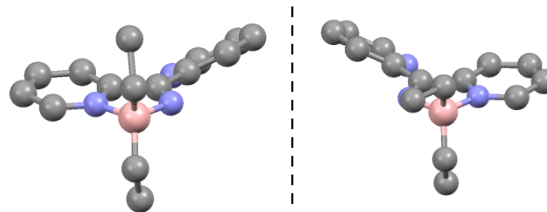


Fig. ESI-2 The two crystallographically independent molecules of **4c** in the asymmetric unit, illustrating the non-crystallographic mirror plane.

Computational studies

Single point and geometry-optimised DFT calculations were undertaken on the structure of **4b**-BF₃ as determined by X-ray diffraction using the Pople 6-311G* triple zeta basis set⁹ and the B3LYP functional¹⁰ within Jaguar.¹¹ Geometry optimisations were performed with bond elongation constraints along the N-BF₃ vector in 0.2 Å increments but failed to reveal a transition state. The pK_{b} of **4c** was determined from the value derived using the quantum mechanical pK_{a} prediction module in Jaguar based on **4c**-H⁺ in water. NBO analysis was undertaken on **4b**-BF₃ and revealed strong polarisation of the B-N bonds in the sense B^{δ+}-N^{δ-} in accord with electronegativity differences between B and N. The NBO analysis

revealed significant delocalisation and both the partial charges and formal NBO bond orders in the bicyclic core are shown in ESI Fig. 3.

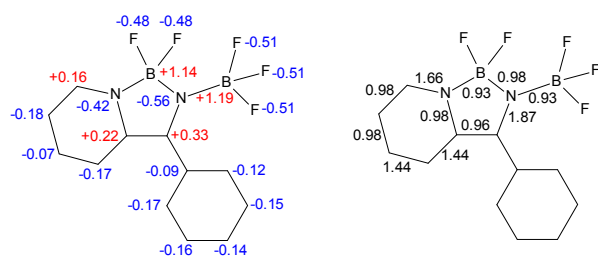


Fig. ESI-3 NBO charges (left) and bond orders (right) for **4b**·BF₃

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Table ESI-1 Crystal data for compounds **4a**·HCl·THF, **4b**·BF₃ and **4c**·HCl·THF

	4a ·HCl·THF	4b ·BF ₃	4c ·HCl·THF
Formula	C ₁₆ H ₂₀ BN ₂ ·C ₄ H ₈ O·Cl	C ₁₂ H ₉ B ₂ F ₃ N ₂	C ₁₅ H ₁₉ BN ₃ ·C ₄ H ₈ O·Cl
FW	358.70	297.83	359.71
Temp. (K)	240(2)	173(2)	180(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁</i>
<i>a</i> /Å	9.2150(2)	9.934(3)	9.38350(10)
<i>b</i> /Å	13.4773(3)	12.290(4)	12.8596(3)
<i>c</i> /Å	17.1221(4)	21.001(7)	16.6196(3)
<i>α</i> /°	90.00	90.00	90.00
<i>β</i> /°	97.697(2)	90.00	99.1807(12)
<i>γ</i> /°	90.00	90.00	90.00
<i>V</i> /Å ³	2107.29(8)	2564.0(14)	1979.77(6)
<i>Z</i>	4	8	4
<i>D_c</i> /Mg m ⁻³	1.131	1.543	1.207
<i>μ</i> (Mo-Kα)/cm ⁻¹	0.191	0.142	0.204
Total reflections	21422	25423	25481
Unique Reflections	6052	2957	7194
Reflns [<i>I</i> >2σ(<i>I</i>)]	3359	2480	6037
<i>θ</i> range	3.76 ≤ <i>θ</i> ≤ 29.98	1.94 ≤ <i>θ</i> ≤ 27.88	2.69 ≤ <i>θ</i> ≤ 26.37
<i>R</i> _{int}	0.055	0.052	0.051
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	0.093, 0.179	0.048, 0.139	0.045, 0.106
Residual <i>e</i> /Å ³	+0.50/-0.48	+0.49/-0.20	+0.30/-0.34