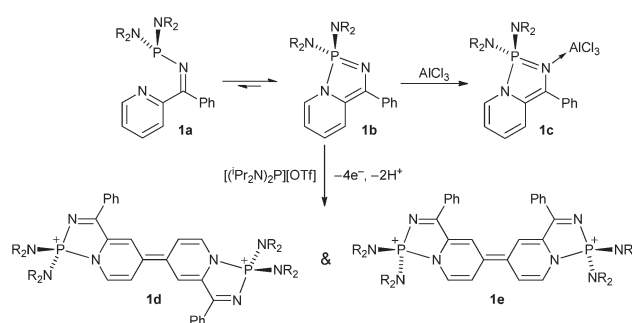## COMMUNICATION

Intramolecular N-coordination in ketiminoboranes†‡

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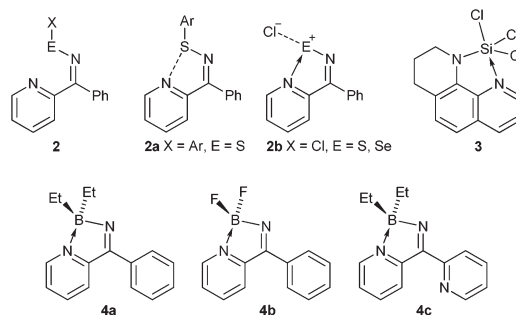**Treatment of the imine PhC(=NSiMe₃)py with Et₂BOMe or BF₃·Et₂O afforded bicyclic ketiminoboranes 4a and 4b via intramolecular N-coordination. The basicity of the imine N is evidenced by their reactivity towards Brønsted and Lewis acids and the structures of 4a·HCl and 4b·BF₃ are reported as well as the dipyridyl imine derivative 4c·HCl.**

The use of intramolecular coordination of a pyridyl group has been exploited in recent years as a route to novel main group heterocycles. For example Dyer and co-workers investigated the intramolecular N-coordination of 2-pyridyl-*N*-phosphino-imines (**1**) and found that an equilibrium existed between open and closed forms **1a** and **1b**.[1] The 2-coordinate nitrogen in **1b** is found to be sufficiently basic to form the adduct **1c** with Lewis acidic AlCl₃,[1] whilst oxidation with [(ᶦPr₂N)₂P][OTf] led to an unusual π-conjugated coupled products (**1d** and **1e**) (Scheme 1) *via* an oxidative radical coupling process.[2]

Studies on the chemistry of related group 16 compounds revealed similar behaviour between ring-open and ring-closed products (Scheme 2). For example, when X = Ar (E = S) the open-form **2a** is favoured with a short intramolecular S···N contact whereas when X = Cl (E = S, Se) then the ring-closed form **2b** was favoured.[3] Work by Brusso and co-workers has revealed that at elevated temperatures ring-opening of these N-bridgehead thiadiazoles can occur.[4] Similar intramolecular N-coordination has been implemented to generate hypervalent Siᴵⱽ (**3**).[5]

Scheme 1

Scheme 2

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In these compounds the group 14/15/16 heteroatoms are all formally electron precise centres and intramolecular N-coordination makes them hypervalent affording some degree of lability between open and closed forms. Conversely group 13 elements are Lewis acidic and ring closure is expected to be strongly favoured. Ketiminoboranes, R₂C=N-BR₂ were reported by Hawthorne, Wade and Lappert in the 1960's and are variously monomeric or dimeric depending upon substituents, with the monomeric ketimines R₂C=NBR₂ formally isoelectronic with allene.[6] In the current manuscript we describe the synthesis of ketiminoboranes in which the R group is capable of intramolecular coordination forming novel C/N/B heterocycles (**4a–c**). These heterocycles are similar to

N,N′-boron chelate complexes, particularly derivatives of BODIPY, which have attracted considerable attention for their fluorescent properties,[7] as dyes in photodynamic therapy,[8] as well as photo-induced electron and energy transfer[9] and as optical switches[10] *inter alia*. In the current paper we describe the generation of **4a–4c** and find that the 2-coordinate imine nitrogen is strongly basic, permitting us to isolate and structurally characterise **4a·HCl**, and **4b·BF₃** and **4c·HCl**.§

Compounds **4a–4c** were prepared using a similar condensation reaction to that employed by Wade[6e] to prepare Ph₂C=NBPh₂ *i.e. via* the condensation of the imine Ar₂C=NSiMe₃ with either Et₂BOMe or BF₃·OEt₂. Crystals of **4a·HCl** and **4c·HCl** appeared over 3 days and were isolated by filtration (27–37% unoptimised isolated yield). The HCl presumably arises from adventitious hydrolysis of Me₃SiCl. Crystals of **4b·BF₃** were initially recovered in low yield from the reaction of PhC(=NSiMe₃)py with BF₃·Et₂O in a 1 : 1 ratio but substantially improved yields (61%) were achieved using a 1 : 2 ratio. This suggests that the low solubility of the adduct favours crystallisation of the 1 : 2 product.

The ^{1}H NMR spectrum of **4a·HCl** clearly reveals a broad singlet at 16.3 ppm consistent with N-protonation whilst the ^{11}B NMR spectrum revealed a singlet at +8 ppm consistent with a tetrahedral B centre and a molecular ion peak at m/z = 251 with an isotope distribution pattern consistent with **4a·H⁺**. The structure of **4a·HCl** was determined by X-ray diffraction (Fig. 1) and found to crystallise as a THF solvate. The B–C bonds are unexceptional but the B–N bond lengths are slightly different (within 3 esd's) with the B1–N1 bond (1.561(5) Å) somewhat shorter than the formally dative pyridyl B–N bond (1.595(5) Å). Both are consistent with B–N single bond character (1.57–1.60 Å).[11] The C10–N1 bond at 1.285(4) is short, consistent with significant imine character. At 3.058(3) Å the N1···Cl1 distance is consistent with a conventional N–H···Cl hydrogen-bonded contact.[12]

The ^{11}B and ^{19}F spectra of **4b·BF₃** revealed *four* ^{19}F and *four* ^{11}B NMR resonances, the intensities of which varied depending upon solvent. In the ^{11}B NMR in MeCN *two* triplet resonances are observed in the 4–8 ppm range corresponding to two chemically distinct BF₂ environments, comparable with other
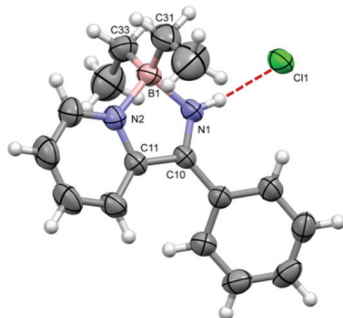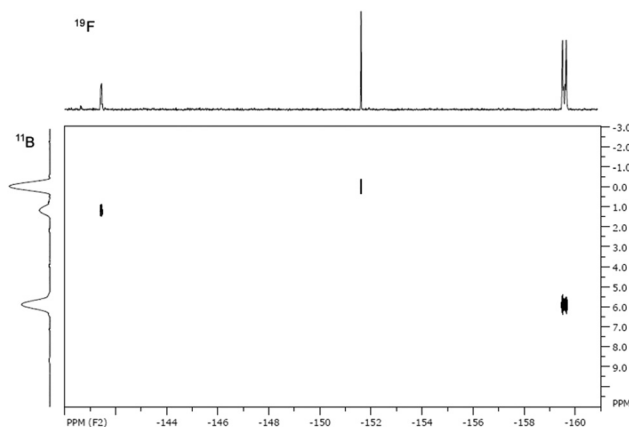

Fig. 2 ^{11}B–^{19}F HMQC NMR spectra of **4b·BF₃** in MeCN.

4-coordinate BN₂F₂ centres.[10,13] In addition, a quartet at 0 ppm and a singlet at −1 ppm are observed (see ESI†). The quartet we tentatively assign to the N-coordinated BF₃ in **4b·BF₃** and the singlet as BF₃·MeCN, based on chemical shift. These observations suggest a dynamic equilibrium (eqn (1)) in which the coordinated BF₃ is labile in the presence of coordinating solvents. In the ^{19}F NMR three resonances exhibit ^{11}B hyperfine coupling (see ESI†) and the HMQC 2D NMR spectrum (Fig. 2) along with coupling constants confirms the assignments of the corresponding BF₂ and BF₃ groups. In the ^{19}F NMR spectrum in MeCN the BF₂ fluorine atoms in both **4b** and **4b·BF₃** appear around −159 ppm, reflecting very similar chemical environments whereas the BF₃ resonances appear at −152 ppm (BF₃·MeCN) and −141 ppm (**4b·BF₃**). The resonance at −152 ppm appears as two signals in an approximate 4 : 1 ratio separated by 0.3 ppm and reflects the ^{11}B and ^{10}B isotopomers (~80 : 20 natural abundance). In non-coordinating solvents such as benzene just two ^{11}B resonances are detected suggesting displacement of BF₃ in non-coordinating solvents is unfavourable and the structure of **4b·BF₃** appears fully retained in solution.

$$\text{(1)}$$
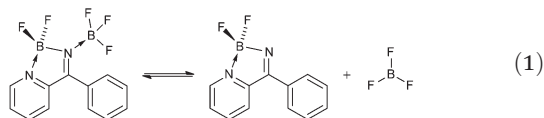
Crystals of **4b·BF₃** were grown from the mother liquor on standing for 24–48 h. Single crystal structure determination revealed one molecule per asymmetric unit (Fig. 3). The heterocyclic C₂N₂B ring exhibits a similar geometry to the ethyl derivative with a longer B–N bond to the pyridyl nitrogen (1.600(2) Å) than to the imine nitrogen (1.574(2) Å) and a short imine-like C=N bond (1.286(2) Å). These distances fall at the extremes of those reported previously for other C₂N₂B heterocycles with a pyridyl nitrogen atom coordinated to a BF₂ group in which the dative bonds fall in the range 1.60–1.63 Å and the covalent B–N bonds fall in the range 1.50–1.57 Å.[9,12] The *exo*

Fig. 1 Molecular structure of **4a·HCl** (THF solvent omitted for clarity) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths: B1–C31 1.598(6), B1–C33 1.598(5), B1–N1 1.561(5), B1–N2 1.595(5), N1–C10 1.285(4), N2–C11 1.355(4), C10–C11 1.476(4) Å.
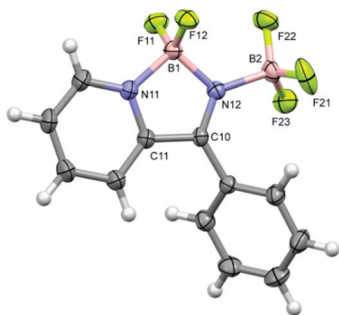
Fig. 3 Molecular structure of **4b**·BF$_3$ with ellipsoids drawn at the 50% probability level. Selected bond lengths: B1–F11 1.366(2), B1–F12 1.364(2), B1–N11 1.600(2), B1–N12 1.574(2), N11–C11 1.349(2), C10–N12 1.286(2), C10–C11 1.490(2), N12–B2 1.600(2) B2–F21 1.377(2), B2–F22 1.377(2), B2–F23 1.366(2) Å.

B–N dative bond length to the BF$_3$ group, at 1.600(2) Å, is identical to the dative pyridyl-N–B bond.

Theoretical calculations (DFT B3LYP/6-311G*) on the reaction of **4b** with BF$_3$ indicate adduct formation in the gas phase is favoured by 75 kJ mol^{-1} (see ESI†). Additional calculations along the B⋯N bond forming pathway reveal no significant activation energy barrier to formation of **4b**·BF$_3$. However stabilisation of the 'free' BF$_3$ in coordinating solvents through adduct formation such as MeCN·BF$_3$ or THF·BF$_3$ is expected to destabilise **4b**·BF$_3$ with respect to loss of BF$_3$. An NBO analysis revealed a bonding pattern best represented by the figure shown for **4b**·BF$_3$ (eqn (1)) (see ESI†). Notably the reaction of py$_2$C=O with Li[N(SiMe$_3$)$_2$]/Me$_3$SiCl, followed by 1 equivalent of Et$_2$BOMe afforded the pyridyl analogue, **4c**·HCl in which the diazaborole nitrogen is protonated rather than the pyridyl nitrogen atom, reflecting the strongly basic nature of the diazaborole nitrogen atom (pK_b = 5.6, calculated using DFT methods), cf. pyridine (pK_b = 8.8).[14] Synthetic details and crystallographic data for **4c**·HCl are available as ESI.†

The current studies reflect the diversity of heterocyclic ring systems accessible by intramolecular N-coordination. Unlike the later p-block elements in which intramolecular coordination generates a hypervalent multi-centre bonding interaction, the electron poor boron centre adopts a 4-coordinate electron-precise centre upon intramolecular coordination. The resultant heterocycle offers a strongly basic nitrogen atom which affords similar acid–base chemistry to the N-pyridyl phosphine-imines.

Acknowledgements

Notes and references

§Crystal data for **4a**·HCl·THF monoclinic space group P2$_1$/c, M = 358.70, T = 240(2) K, a = 9.2150(2), b = 13.4773(3), c = 17.1221(4) Å, b = 97.697(2)°, V = 2107.29(8) Å^3, Z = 4, D$_c$ = 1.131 g cm^{-3}, μ(Mo-Kα) = 0.191 mm^{-1}. 21 422 reflections measured (3.76 ≤ 2θ ≤ 29.98°) of which 6052 unique (R$_{int}$ = 0.055). Final R$_1$ (I > 2σ(I)) = 0.093, wR$_2$ (all data) = 0.179 for 214 parameters. Max/min electron density +0.50/−0.48 e$^-$ Å^{-3}.

Crystal data for **4b**·BF$_3$ orthorhombic space group Pbca, M = 297.83, T = 173(2) K, a = 9.934(3), b = 12.290(4), c = 21.001(7) Å, V = 2564.0(14) Å^3, Z = 8, D$_c$ = 1.543 g cm^{-3}, μ(Mo-Kα) = 0.142 mm^{-1}. 25 423 reflections measured (1.94 ≤ 2θ ≤ 27.88°) of which 2957 unique (R$_{int}$ = 0.052). Final R$_1$ (I > 2σ(I)) = 0.048, wR$_2$ (all data) = 0.139 for 197 parameters. Max/min electron density +0.49/−0.20 e$^-$ Å^{-3}.

Crystal data for **4c**·HCl·THF monoclinic space group P2$_1$, M = 359.71, T = 180(2) K, a = 9.38350(10), b = 12.8596(3), c = 16.6196(3) Å, β = 99.1807(12)°, V = 1979.77(6) Å^3, Z = 4, D$_c$ = 1.207 g cm^{-3}, μ(Mo-Kα) = 0.204 mm^{-1}. 25 481 reflections measured (2.69 ≤ 2θ ≤ 26.37°) of which 7194 unique (R$_{int}$ = 0.051). Final R$_1$ (I > 2σ(I)) = 0.045, wR$_2$ (all data) = 0.106 for 453 parameters. Max/min electron density +0.30/−0.34 e$^-$ Å^{-3}.

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