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# Intramolecular N -coordination in ketiminoboranes $\dagger \ddagger$ 

Catherine E. Bacon, ${ }^{\text {a }}$ Liz Mansour, ${ }^{\text {b }}$ John J. Hayward ${ }^{\text {b }}$ and Jeremy M. Rawson* ${ }^{\text {b }}$

Treatment of the imine $\mathrm{PhC}\left(=\mathrm{NSiMe}_{3}\right)$ py with $\mathrm{Et}_{2} \mathrm{BOMe}$ or $\mathrm{BF}_{3} \cdot \mathrm{Et}_{2} \mathrm{O}$ afforded bicyclic ketiminoboranes 4 a and 4 b via intramolecular N -coordination. The basicity of the imine N is evidenced by their reactivity towards Brønsted and Lewis acids and the structures of $4 \mathrm{a} \cdot \mathrm{HCl}$ and $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ are reported as well as the dipyridyl imine derivative $4 \mathrm{c} \cdot \mathrm{HCl}$.

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 -phosphinoimines (1) and found that an equilibrium existed between open and closed forms $\mathbf{1 a}$ and $\mathbf{1 b} .{ }^{1}$ The 2-coordinate nitrogen in $\mathbf{1 b}$ is found to be sufficiently basic to form the adduct $\mathbf{1 c}$ with Lewis acidic $\mathrm{AlCl}_{3},{ }^{1}$ whilst oxidation with $\left[\left({ }^{\mathrm{i}} \mathrm{Pr}_{2} \mathrm{~N}\right)_{2} \mathrm{P}\right][\mathrm{OTf}]$ led to an unusual $\pi$-conjugated coupled products ( $\mathbf{1 d}$ and $\mathbf{1 e}$ ) (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 $\mathrm{X}=\operatorname{Ar}(\mathrm{E}=\mathrm{S})$ the open-form 2 a is favoured with a short intramolecular $\mathrm{S} \cdots \mathrm{N}$ contact whereas when $\mathrm{X}=\mathrm{Cl}(\mathrm{E}=\mathrm{S}, \mathrm{Se})$ 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 $\mathrm{Si}^{\mathrm{IV}}(3) .{ }^{5}$

[^0]

Scheme 1


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, $\quad \mathrm{R}_{2} \mathrm{C}=\mathrm{N}-\mathrm{BR}_{2} \quad$ were reported by Hawthorne, Wade and Lappert in the 1960's and are variously monomeric or dimeric depending upon substituents, with the monomeric ketimines $\mathrm{R}_{2} \mathrm{C}=\mathrm{NBR}_{2}$ 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 $\mathrm{C} / \mathrm{N} / \mathrm{B}$ heterocycles ( $\mathbf{4 a - c}$ ). These heterocycles are similar to
$N, N^{\prime}$-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 $\mathbf{4 a - 4} \mathbf{c}$ and find that the 2 -coordinate imine nitrogen is strongly basic, permitting us to isolate and structurally characterise $\mathbf{4 a} \cdot \mathrm{HCl}$, and $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ and $\mathbf{4 c} \cdot \mathrm{HCl}$.§

Compounds $\mathbf{4 a}-\mathbf{4 c}$ were prepared using a similar condensation reaction to that employed by Wade ${ }^{6 e}$ to prepare $\mathrm{Ph}_{2} \mathrm{C}=\mathrm{NBPh}_{2}$ i.e. via the condensation of the imine $\mathrm{Ar}_{2} \mathrm{C}=\mathrm{NSiMe}_{3}$ with either $\mathrm{Et}_{2} \mathrm{BOMe}$ or $\mathrm{BF}_{3} \mathrm{OEt}_{2}$. Crystals of $\mathbf{4 a} \cdot \mathrm{HCl}$ and $\mathbf{4 c} \cdot \mathrm{HCl}$ appeared over 3 days and were isolated by filtration ( $27-37 \%$ unoptimised isolated yield). The HCl presumably arises from adventitious hydrolysis of $\mathrm{Me}_{3} \mathrm{SiCl}$. Crystals of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ were initially recovered in low yield from the reaction of $\mathrm{PhC}\left(=\mathrm{NSiMe}_{3}\right)$ py with $\mathrm{BF}_{3} \cdot \mathrm{Et}_{2} \mathrm{O}$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{4 a} \cdot \mathrm{HCl}$ clearly reveals a broad singlet at 16.3 ppm consistent with N -protonation whilst the
${ }^{11} \mathrm{~B}$ 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 $\mathbf{4 a} \cdot \mathrm{H}^{+}$. The structure of $\mathbf{4 a} \cdot \mathrm{HCl}$ was determined by X-ray diffraction (Fig. 1) and found to crystallise as a THF solvate. The B-C bonds are unexceptional but the $\mathrm{B}-\mathrm{N}$ bond lengths are slightly different (within 3 esd's) with the B1-N1 bond (1.561(5) $\AA$ ) somewhat shorter than the formally dative pyridyl $\mathrm{B}-\mathrm{N}$ bond (1.595(5) Å). Both are consistent with B-N single bond character (1.57-1.60 $\AA$ ). ${ }^{11}$ The C10-N1 bond at 1.285(4) is short, consistent with significant imine character. At $3.058(3) \AA$ the $\mathrm{N} 1 \cdots \mathrm{Cl} 1$ distance is consistent with a conventional $\mathrm{N}-\mathrm{H} \cdots \mathrm{Cl}$ hydrogen-bonded contact. ${ }^{12}$

The ${ }^{11} \mathrm{~B}$ and ${ }^{19} \mathrm{~F}$ spectra of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ revealed four ${ }^{19} \mathrm{~F}$ and four ${ }^{11} \mathrm{~B}$ NMR resonances, the intensities of which varied depending upon solvent. In the ${ }^{11} \mathrm{~B}$ NMR in MeCN two triplet resonances are observed in the $4-8 \mathrm{ppm}$ range corresponding to two chemically distinct $\mathrm{BF}_{2}$ environments, comparable with other


Fig. 1 Molecular structure of $\mathbf{4 a} \cdot \mathrm{HCl}$ (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. $2{ }^{11} \mathrm{~B}-{ }^{19} \mathrm{~F}$ HMQC NMR spectra of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ in MeCN .

4-coordinate $\mathrm{BN}_{2} \mathrm{~F}_{2}$ centres. ${ }^{10,13}$ In addition, a quartet at 0 ppm and a singlet at -1 ppm are observed (see ESI $\dagger$ ). The quartet we tentatively assign to the N -coordinated $\mathrm{BF}_{3}$ in $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ and the singlet as $\mathrm{BF}_{3} \mathrm{MeCN}$, based on chemical shift. These observations suggest a dynamic equilibrium (eqn (1)) in which the coordinated $\mathrm{BF}_{3}$ is labile in the presence of coordinating solvents. In the ${ }^{19} \mathrm{~F}$ NMR three resonances exhibit ${ }^{11} \mathrm{~B}$ hyperfine coupling (see ESI $\dagger$ ) and the HMQC 2D NMR spectrum (Fig. 2) along with coupling constants confirms the assignments of the corresponding $\mathrm{BF}_{2}$ and $\mathrm{BF}_{3}$ groups. In the ${ }^{19} \mathrm{~F}$ NMR spectrum in MeCN the $\mathrm{BF}_{2}$ fluorine atoms in both $\mathbf{4 b}$ and $\mathbf{4} \mathbf{b} \cdot \mathrm{BF}_{3}$ appear around -159 ppm , reflecting very similar chemical environments whereas the $\mathrm{BF}_{3}$ resonances appear at $-152 \mathrm{ppm}\left(\mathrm{BF}_{3} \cdot \mathrm{MeCN}\right)$ and $-141 \mathrm{ppm}\left(\mathbf{4 b} \cdot \mathrm{BF}_{3}\right)$. The resonance at -152 ppm appears as two signals in an approximate $4: 1$ ratio separated by 0.3 ppm and reflects the ${ }^{11} \mathrm{~B}$ and ${ }^{10} \mathrm{~B}$ isotopomers ( $\sim 80: 20$ natural abundance). In non-coordinating solvents such as benzene just two ${ }^{11} \mathrm{~B}$ resonances are detected suggesting displacement of $\mathrm{BF}_{3}$ in non-coordinating solvents is unfavourable and the structure of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ appears fully retained in solution.


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


Fig. 3 Molecular structure of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ 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 $\mathrm{BF}_{3}$ group, at $1.600(2) \AA$, is identical to the dative pyridyl-N-B bond.

Theoretical calculations (DFT B3LYP/6-311G*) on the reaction of $\mathbf{4 b}$ with $\mathrm{BF}_{3}$ indicate adduct formation in the gas phase is favoured by $75 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (see ESI $\dagger$ ). Additional calculations along the $\mathrm{B} \cdots \mathrm{N}$ bond forming pathway reveal no significant activation energy barrier to formation of $\mathbf{4 b} \cdot \mathrm{BF}_{3}$. However stabilisation of the 'free' $\mathrm{BF}_{3}$ in coordinating solvents through adduct formation such as $\mathrm{MeCN} \cdot \mathrm{BF}_{3}$ or THF $\cdot \mathrm{BF}_{3}$ is expected to destabilise $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ with respect to loss of $\mathrm{BF}_{3}$. An NBO analysis revealed a bonding pattern best represented by the figure shown for $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ (eqn (1)) (see ESI $\dagger$ ). Notably the reaction of $\mathrm{py}_{2} \mathrm{C}=\mathrm{O}$ with $\mathrm{Li}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right] / \mathrm{Me}_{3} \mathrm{SiCl}$, followed by 1 equivalent of $\mathrm{Et}_{2} \mathrm{BOMe}$ afforded the pyridyl analogue, $\mathbf{4 c} \cdot \mathrm{HCl}$ in which the diazaborole nitrogen is protonated rather than the pyridyl nitrogen atom, reflecting the strongly basic nature of the diazaborole nitrogen atom $\left(\mathrm{p} K_{\mathrm{b}}=5.6\right.$, calculated using DFT methods), $c f$. pyridine ( $\mathrm{p} K_{\mathrm{b}}=8.8$ ). ${ }^{14}$ Synthetic details and crystallographic data for $\mathbf{4 c} \cdot \mathrm{HCl}$ are available as ESI. $\dagger$

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.

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## Notes and references

$\S$ Crystal data for $\mathbf{4 a} \cdot \mathrm{HCl} \cdot \mathrm{THF}$ monoclinic space group $P 2_{1} / c, M=358.70$. $T=$ $240(2) \mathrm{K}, a=9.2150(2), b=13.4773(3), c=17.1221(4) \AA, b=97.697(2)^{\circ}, V=$ $2107.29(8) \AA^{3}, Z=4, D_{\mathrm{c}}=1.131 \mathrm{~g} \mathrm{~cm}^{-3}, \mu(\mathrm{Mo}-\mathrm{K} \alpha)=0.191 \mathrm{~mm}^{-1} .21422$ reflections measured $\left(3.76 \leq 2 \theta \leq 29.98^{\circ}\right)$ of which 6052 unique ( $R_{\mathrm{int}}=0.055$ ). Final $R_{1}$ $(I>2 \sigma(I))=0.093, \mathrm{w} R_{2}$ (all data) $=0.179$ for 214 parameters. Max/min electron density $+0.50 /-0.48 \mathrm{e}^{-} \AA^{-3}$.

Crystal data for $\mathbf{4 b} \cdot \mathrm{BF}_{3}$ orthorhombic space group $P b c a, M=$ 297.83. $T=173(2)$ $\mathrm{K}, a=9.934(3), b=12.290(4), c=21.001(7) \AA, V=2564.0(14) \AA^{3}, Z=8, D_{\text {c }}=$ $1.543 \mathrm{~g} \mathrm{~cm}^{-3}, \mu(\mathrm{Mo}-\mathrm{K} \alpha)=0.142 \mathrm{~mm}^{-1} .25423$ reflections measured $(1.94 \leq 2 \theta \leq$ $27.88^{\circ}$ ) of which 2957 unique ( $R_{\text {int }}=0.052$ ). Final $R_{1}(I>2 \sigma(I))=0.048, \mathrm{w} R_{2}$ (all data) $=0.139$ for 197 parameters. Max/min electron density $+0.49 /-0.20 \mathrm{e}^{-} \AA^{-3}$.

Crystal data for $\mathbf{4 c} \cdot \mathrm{HCl} \cdot \mathrm{THF}$ monoclinic space group $P 2_{1}, M=359.71$. $T=$ $180(2) \mathrm{K}, a=9.38350(10), b=12.8596(3), c=16.6196(3) \AA, \beta=99.1807(12)^{\circ}, V=$ $1979.77(6) \AA^{3}, Z=4, D_{\mathrm{c}}=1.207 \mathrm{~g} \mathrm{~cm}^{-3}, \mu(\mathrm{Mo}-\mathrm{K} \alpha)=0.204 \mathrm{~mm}^{-1} .25481$ reflections measured $\left(2.69 \leq 2 \theta \leq 26.37^{\circ}\right)$ of which 7194 unique ( $R_{\mathrm{int}}=0.051$ ). Final $R_{1}$ $(I>2 \sigma(I))=0.045, \mathrm{w} R_{2}$ (all data) $=0.106$ for 453 parameters. Max/min electron density $+0.30 /-0.34 \mathrm{e}^{-} \AA^{-3}$.

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[^0]:    ${ }^{a}$ Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
    ${ }^{b}$ Department of Chemistry \& Biochemistry, The University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada N9B 3P4. E-mail: jmrawson@uwindsor.ca $\dagger$ In memory of Ken Wade: Teacher, oft-times mentor, colleague and friend. His contributions in the field of structure and bonding in main group chemistry will continue into the future, but his guidance, encouragement and support for so many of the young academics he came in contact with will be sorely missed.
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