Dalton Transactions

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 5284

Received 15th January 2015,
Accepted 13th February 2015

DOI: 10.1039/c5dt00196j

www.rsc.org/dalton

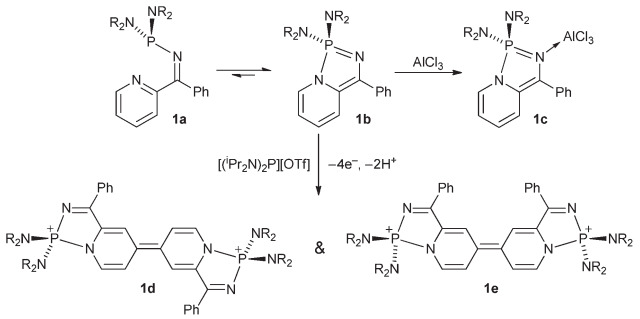
Intramolecular N-coordination in ketiminoboranes†‡

Catherine E. Bacon,[a] Liz Mansour,[b] John J. Hayward[b] and Jeremy M. Rawson*[b]

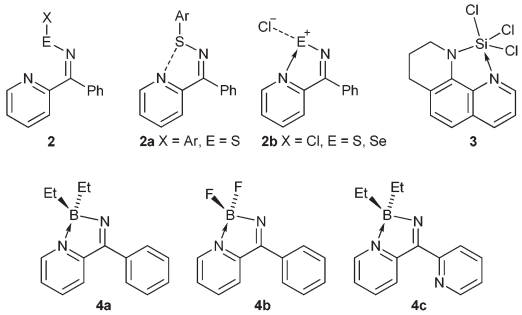
Treatment of the imine PhC(=NSiMe$_3$)py with Et$_2$BOMe or BF$_3$·Et$_2$O afforded bicyclic ketiminoboranes 4a and 4b *via* intramolecular N-coordination. The basicity of the imine N is evidenced by their reactivity towards Brønsted and Lewis acids and the structures of 4a·HCl and 4b·BF$_3$ are reported 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*-phosphinoimines (**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 $AlCl_3$,[1] whilst oxidation with $[(^iPr_2N)_2P][OTf]$ 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 Si^{IV} (**3**).[5]



Scheme 1



Scheme 2

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, $R_2C{=}N\text{-}BR_2$ were reported by Hawthorne, Wade and Lappert in the 1960's and are variously monomeric or dimeric depending upon substituents, with the monomeric ketimines $R_2C{=}NBR_2$ 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 C/N/B heterocycles (**4a–c**). These heterocycles are similar to

[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*

† 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.

‡ Electronic supplementary information (ESI) available: Full experimental details, details of the computational and crystallographic studies and crystallographic data in cif format. CCDC 1043411–1043413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00196j

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**·BF_3 and **4c**·HCl.§

Compounds **4a–4c** were prepared using a similar condensation reaction to that employed by Wade[6e] to prepare $Ph_2C{=}NBPh_2$ *i.e. via* the condensation of the imine $Ar_2C{=}NSiMe_3$ with either Et_2BOMe or BF_3 OEt_2. 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 Me_3SiCl. Crystals of **4b**·BF_3 were initially recovered in low yield from the reaction of $PhC(=NSiMe_3)py$ with $BF_3{\cdot}Et_2O$ 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**·BF_3 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 BF_2 environments, comparable with other

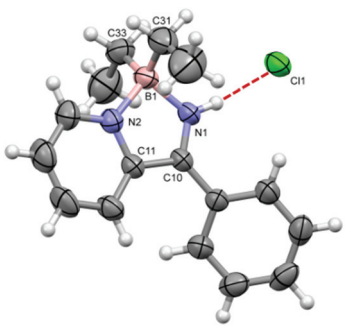


Fig. 1 Molecular structure of **4a**·HCl (THF solvent omitted for clarity) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths: B1–C31 1.598(6), B1–C33 1.598(5), B1–N1 1.561(5), B1–N2 1.595(5), N1–C10 1.285(4), N2–C11 1.355(4), C10–C11 1.476(4) Å.

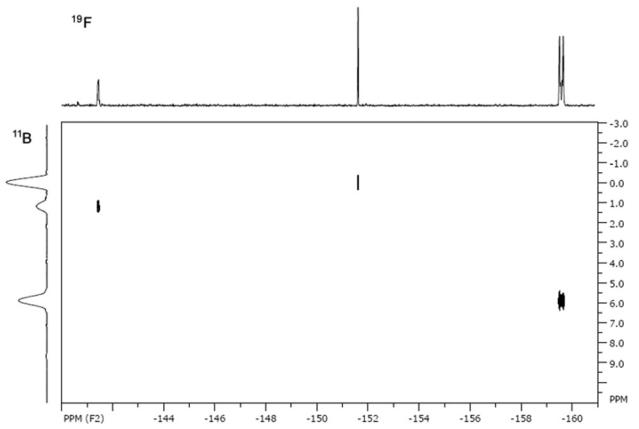
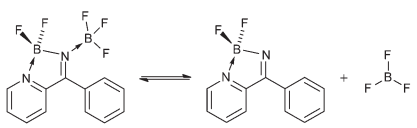


Fig. 2 ^{11}B–^{19}F HMQC NMR spectra of **4b**·BF_3 in MeCN.

4-coordinate BN_2F_2 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 BF_3 in **4b**·BF_3 and the singlet as BF_3 MeCN, based on chemical shift. These observations suggest a dynamic equilibrium (eqn (1)) in which the coordinated BF_3 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 BF_2 and BF_3 groups. In the ^{19}F NMR spectrum in MeCN the BF_2 fluorine atoms in both **4b** and **4b**·BF_3 appear around −159 ppm, reflecting very similar chemical environments whereas the BF_3 resonances appear at −152 ppm (BF_3·MeCN) and −141 ppm (**4b**·BF_3). 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 BF_3 in non-coordinating solvents is unfavourable and the structure of **4b**·BF_3 appears fully retained in solution.



(1)

Crystals of **4b**·BF_3 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 C_2N_2B 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 C_2N_2B heterocycles with a pyridyl nitrogen atom coordinated to a BF_2 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*

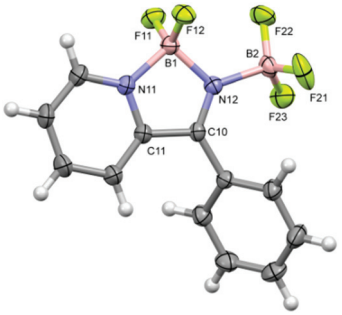


Fig. 3 Molecular structure of **4b**·BF_3 with ellipsoids drawn at the 50% probability level. Selected bond lengths: B1–F11 1.366(2), B1–F12 1.364(2), B1–N11 1.600(2), B1–N12 1.574(2), N11–C11 1.349(2), C10–N12 1.286(2), C10–C11 1.490(2), N12–B2 1.600(2) B2–F21 1.377(2), B2–F22 1.377(2), B2–F23 1.366(2) 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 $py_2C{=}O$ with $Li[N(SiMe_3)_2]$/Me_3SiCl, followed by 1 equivalent of Et_2BOMe 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

We would like to thank EPSRC (C.E.B.), NSERC and the Canada Research Chairs program (J.J.H.) and the University of Windsor (L.M.) for financial support. In addition we are indebted to Dr M. Revington for assistance with the 2D multinuclear NMR studies.

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 ($3.76 \leq 2\theta \leq 29.98°$) of which 6052 unique ($R_{int}$ = 0.055). Final R_1 ($I > 2\sigma(I)$) = 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 ($1.94 \leq 2\theta \leq 27.88°$) of which 2957 unique ($R_{int}$ = 0.052). Final R_1 ($I > 2\sigma(I)$) = 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 ($2.69 \leq 2\theta \leq 26.37°$) of which 7194 unique ($R_{int}$ = 0.051). Final R_1 ($I > 2\sigma(I)$) = 0.045, wR_2 (all data) = 0.106 for 453 parameters. Max/min electron density +0.30/−0.34 e^- $Å^{-3}$.

1 D. A. Smith, A. S. Batsanov, K. Miqueu, J.-M. Sotiropoulos, D. C. Apperley, J. A. K. Howard and P. Dyer, *Angew. Chem., Int. Ed.*, 2008, **47**, 8674.
2 D. A. Smith, A. S. Batsanov, M. A. Fox, A. Beeby, D. C. Apperley, J. A. K. Howard and P. Dyer, *Angew. Chem., Int. Ed.*, 2009, **48**, 9109.
3 C. E. Bacon, D. J. Eisler, R. L. Melen and J. M. Rawson, *Chem. Commun.*, 2008, 4924.
4 A. A. Leitch, I. Korobkov, A. Assoud and J. L. Brusso, *Chem. Commun.*, 2014, **50**, 4934.
5 See for example: (*a*) G. Klebe, J. W. Bats and K. Hensen, *J. Chem. Soc., Dalton Trans.*, 1985, 1; (*b*) G. Klebe, J. W. Bats and H. Fuess, *J. Am. Chem. Soc.*, 1984, **106**, 5203.
6 (*a*) M. F. Hawthorne, *Tetrahedron*, 1962, **17**, 117; (*b*) J. E. Lloyd and K. Wade, *J. Chem. Soc.*, 1964, 1649; (*c*) I. Pattison and K. Wade, *J. Chem. Soc. A*, 1967, 1098; (*d*) V. A. Dorokhov and M. F. Lappert, *Chem. Commun.*, 1968, 250; (*e*) J. R. Jennings, I. Pattison, C. Summerford, K. Wade and B. K. Wyatt, *Chem. Commun.*, 1968, 250; (*f*) C. Summerford and K. Wade, *J. Chem. Soc. A*, 1969, 1487; (*g*) C. Summerford and K. Wade, *J. Chem. Soc. A*, 1970, 2010.
7 N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**, 1130; G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.
8 A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77.
9 (*a*) Y. Nagata and Y. Chujo, *Macromol.*, 2008, **41**, 3488; (*b*) C. C. Cheng, W.-S. Yu, P.-T. Chou, S.-M. Peng, G.-H. Lee, P.-C. Wu, Y.-H. Song and Y. Chi, *Chem. Commun.*, 2003, 2628.
10 Y. Yang, R. P. Hughes and I. Aprahamian, *J. Am. Chem. Soc.*, 2012, **134**, 15221.
11 C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry 3rd Edition*, Pearson Ed, Harlow, England, 2008.
12 A search of the CSD (2013) afforded intermolecular hydrogen-bonded N···Cl distances in the range 2.939–3.298 Å (mean 3.12 Å) between three-coordinate N (R_2NH) and Cl^- ions.

13 (*a*) K. Hensen, G. Klebe, J. W. Bats and H. Fuess, *Fresenius' J. Anal. Chem.*, 1982, **312**, 24; (*b*) G. Klebe, K. Hensen and H. Fuess, *Chem. Ber.*, 1983, **116**, 3125; (*c*) J. J. Klappa, S. A. Geers, S. J. Schmidtke, L. A. MacManus-Spencer and K. McNeill, *Dalton Trans.*, 2004, 883; (*d*) M. Mao, S. Xiao, J. Li, Y. Zou, R. Zhang, J. Pan, F. Dan, K. Zou and T. Yi, *Tetrahedron*, 2012, **68**, 5037; (*e*) M. Mao, R. Zhang, S. Xiao and J. Zou, *J. Coord. Chem.*, 2011, **64**, 3303; (*f*) Q. Cao, S. Xiao, M. Mao, X. Chen, S. Wang, L. Li and K. Zou, *J. Organomet. Chem.*, 2012, **717**, 147.

14 N. Tro, T. D. Frigden and L. E. Shaw, *Chemistry: A Molecular Approach, (Canadian Edition)*, Pearson Ed., 2013.