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Two contrasting ethynyl hydroboration pathways in the formation of a novel tris-hydroboration product from reaction of dimesitylborane with 2,5-diethynylpyridine†

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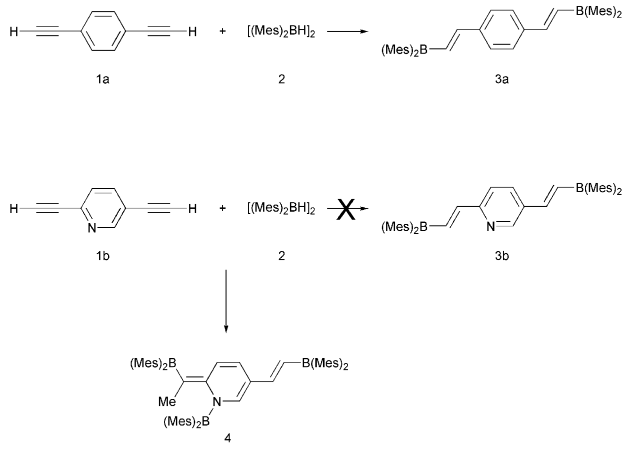
Reaction of 2,5-diethynylpyridine with dimesitylborane, $[(Mes)_2BH]_2$ (Mes = mesityl = 2,4,6-$Me_3C_6H_2$), gave the unexpected tris-hydroboration product 1-{$(Mes)_2B$}-2-[*Z*-1-{$(Mes)_2B$}ethylidene]-5-[*E*-{$(Mes)_2B$}vinyl]-1,2-dihydropyridine, which has been structurally characterised by single-crystal X-ray diffraction.

The vacant p_z orbital on three-coordinate boron provides π-acceptor character, leading to electron-poor compounds which display interesting linear and non-linear optical (NLO) properties.[1] Whilst unsymmetric compounds[2–8] of the form D–X–BR_2 (D = π-donor, X = organic π-system, R = bulky aromatic group) display second-order NLO behaviour,[3,4] strong solvatochromism in their fluorescence spectra,[2–6] electroluminescence[6,7] and two-photon excited fluorescence,[8] symmetric compounds[9–12] of the form R_2B–X–BR_2 display third-order NLO behaviour,[10] can function as fluoride ion sensors[11] and as emitting and/or electron transport/hole-blocking layers in organic light-emitting diodes.[12]

Two bulky mesityl groups (R) on boron generally provide sufficient kinetic stability against hydrolysis, *via* steric shielding of the vacant p orbital, to make the resulting compounds air stable. Typical routes to the symmetric compounds are reaction of Li–X–Li with 2 equiv. of $(Mes)_2BF$, giving $(Mes)_2B$–X–$B(Mes)_2$,[9,10] or di-hydroboration of $HC\equiv C$–X–$C\equiv CH$ (*e.g.* **1a**, X = 1,4-C_6H_4; Scheme 1) with $[(Mes)_2BH]_2$ (**2**),[13] yielding *E*,*E*-$(Mes)_2B$–CH=CH–X–CH=CH–$B(Mes)_2$ (*e.g.* **3a**, X = 1,4-C_6H_4) with excellent stereo- and regioselectivity.[10] Chujo and co-workers[14–16] have extended this approach, employing $HC\equiv C$–X–$C\equiv CH$ with $[RBH_2]_2$ (R = Mes or 2,4,6-$^iPr_3C_6H_2$) to provide electron-poor oligomers or polymers of the form $[–(R)B–CH=CH–X–CH=CH–]_n$, and have reported luminescent[14,15] and third-order NLO[16] behaviour for the resulting materials. One example involved hydroboration polymerisation of 2,5-diethynylpyridine[15] (**1b**). In order to carry out further photophysical studies of the simpler and better characterised diboron compounds **3**, we reacted **1b** with 1 equiv. of **2**, anticipating the formation of **3b** (X = 2,5-pyridinediyl); however, the reaction proceded *via* a different stoichiometry and provided an unusual and unexpected product.



Scheme 1

Dropwise addition, under N_2, of a solution of 1 mmol of **1b** in THF to a solution of 1 mmol of **2** in THF gave an orange solution, which resulted in an orange powder‡ after removal of the solvent. NMR spectra were complex, initially suggesting the presence of a mixture of products. Column chromatography on silica gel, eluting with hexane–acetone 9 : 1, produced a yellow–orange compound, **4**‡, which still gave a ^1H NMR spectrum that was more complex than expected. A single-crystal X-ray diffraction study§ provided the structure of **4** (Fig. 1 and Scheme 1). Whilst the 5-ethynyl group *meta* to N was hydroborated, as expected, in a 1,2-anti-Markovnikov fashion, two other hydroboration reactions took place on the other side of the molecule: (i) a formal 1,2-Markovnikov hydroboration, placing boron on C_α and H on C_β, and (ii) a formal 1,4-hydroboration, placing boron on N and another H on C_β, generating the 2-*exo*-α-borylethylidene function on the 1,2-dihydropyridine ring. The mechanism of the reaction is not yet clear, but a few points are worth considering. Coordination of the pyridine N to dimesitylborane to form intermediate **A** (Scheme 2) is likely, as was observed for $(Mes)_2BF$.[17] In the latter case, subsequent

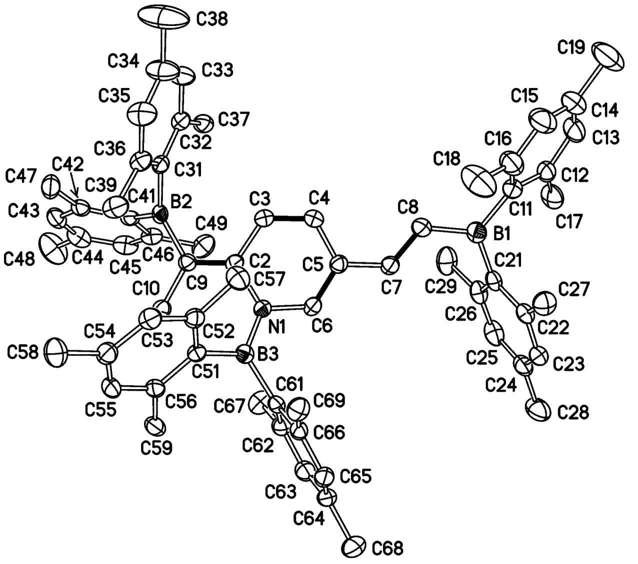


Fig. 1 Molecular structure of **4** with thermal ellipsoids shown at 50% probability, double bonds in solid black and hydrogen atoms omitted for clarity. Selected bond distances (Å): N(1)–C(6) 1.409(2), N(1)–C(2) 1.451(2), N(1)–B(3) 1.453(3), C(2)–C(9) 1.367(3), C(9)–C(10) 1.507(3), C(9)–B(2) 1.573(3), C(2)–C(3) 1.452(3), C(3)–C(4) 1.341(3), C(4)–C(5) 1.444(3), C(5)–C(6) 1.350(3), C(5)–C(7) 1.452(3), C(7)–C(8) 1.349(3), C(8)–B(1) 1.546(3). Torsion angles (°): C(9)–C(2)–N(1)–B(3) −49.9(2), C(31)–B(2)–C(9)–C(2) −42.4(3), C(9)–C(2)–C(3)–C(4) −149.3(2), C(3)–C(4)–C(5)–C(6) −12.9(3), C(6)–C(5)–C(7)–C(8) −171.4(2), C(5)–C(7)–C(8)–B(1) 172.1(2).

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† Electronic supplementary information (ESI) available: NMR data for **4**, rotatable 3-D molecular structure diagrams of optimised geometries in CHIME format and energy data for optimised geometries. See http://www.rsc.org/suppdata/cc/b3/b316250h/

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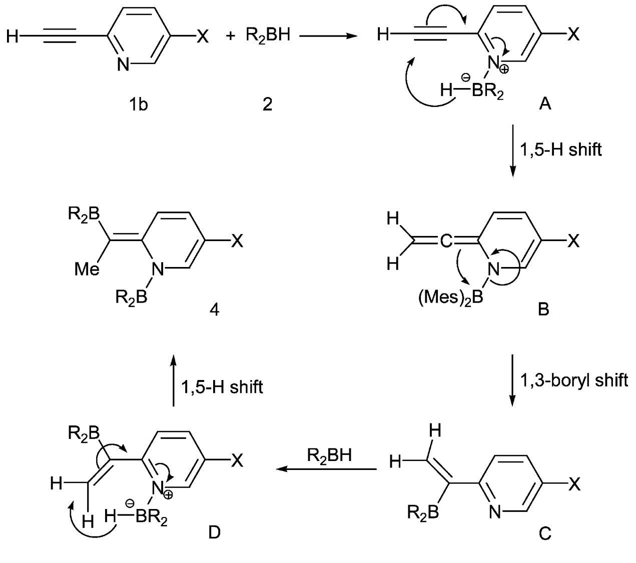

For synthesis: X = C≡C—H or CH=CHBR$_2$; R = Mes
For calculations: X = H; R = 2,6-Me$_2$C$_6$H$_3$

Scheme 2

attack by carbon nucleophiles (RLi) took place at the pyridine C *ortho* to N, with elimination of F$^-$ from B, leading to neutral 1-{B(Mes)$_2$}-2-R-1,2-dihydropyridines (**5**). In our case, this could lead to 1,5-hydride shift to the terminal carbon of the 2-ethynyl moiety, giving propadiene **B**. A subsequent propadiene hydroboration would generally be expected to place boron at the terminal carbon.[18,19] However, a 1,3-boryl shift allows re-aromatisation of the pyridine ring (intermediate **C**) and provides for the overall observed 1,2-Markovnikov alkyne hydroboration. Coordination of a second equivalent of (Mes)$_2$BH to the pyridine N (intermediate **D**) could be followed by another 1,5-hydride shift, yielding the final product, **4**. The mechanism in Scheme 2 is supported by *ab initio* geometry optimisations on compounds **A**–**D** and **4** (X = H, R = 2,6-Me$_2$C$_6$H$_3$). Total energies decrease from **A** to **B** to **C**, indicating that the 1,5-H and 1,3-B shifts in the second and third steps in Scheme 2 are thermodynamically favourable, and model compound **4** is substantially lower in energy than its isomer **D**.

The 1,2-dihydropyridine ring in **4** is, unusually, puckered; C(2), C(3), C(4) and C(5) are coplanar within experimental error, but N(1) and C(6) deviate from this plane by 0.52 and 0.27 Å, respectively. The B(1) and B(2) atoms have trigonal-planar geometries, whilst B(3) and N(1) are somewhat pyramidalised, deviating from trigonal-planar geometries by 0.05 and 0.07 Å, respectively. The twist of 19.5° around the B(3)–N(1) bond reduces the $n(N)\rightarrow p_\pi(B)$ overlap, resulting in a relatively long B–N length of 1.453(3) Å. In **5** (R=Ph),[17] both B and N are planar. The B–N distances in (Mes)$_2$BNHPh[20] and (Mes)$_2$BNH$_2$[21] are 1.407 and 1.375 Å, respectively. Only two structures with a C$_2$B–NC$_2$ moiety (all atoms sp^2 hybridised) have been reported previously: 1,1′-bis(dimesitylboryl)-1,1′,4,4′-tetrahydro-4,4′-bipyridylidene (**6**)[22] and (C$_6$F$_5$)$_2$N–pyrrolylborane (**7**).[23] Molecule **6** resembles **4** in the twist around the B–N bond (18°) and its B–N length of 1.444(3) Å. In planar **7**, the B–N distance is only 1.401(5) Å. Clearly, the geometry of **4** is influenced by severe steric interactions, evident from the large C(9)–C(2)–N(1)–B(3) torsion angle of − 49.9(2)°.

Three inequivalent B(Mes)$_2$ moieties, one exhibiting restricted rotation around the B–C and B–N bonds, and the methyl group on the *exo*-ethylidene moiety account completely for the unexpected complexity of the ^{1}H NMR spectrum of **4**.

A referee pointed out that hydroboration of pyridine is almost unheard of; a recent case of formal 1,4-hydroboration[24] and 1,2- and 1,4-hydroalumination[25] are rare relevant reports. Studies of related reactions and derivatisation of the unusual products will be the subject of future publications.

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Notes and references

‡ Crude yield 0.54 g (92%), purified yield after chromatography 0.35 g (60%) based on boron. Analysis calc'd for $C_{63}H_{74}B_3N$: C 86.21, H 8.50, N 1.60; found: C 85.47, H 8.84, N 1.46%. MS (EI): *m/z* 876 (M − 1).

§ *Crystal data* for **4**: $C_{63}H_{74}B_3N\cdot1.5C_3H_6O\cdot0.5C_6H_{14}$, yellow block (0.31 × 0.23 × 0.11 mm) grown from hexane–acetone, M = 1007.87, triclinic, space group $P\bar{1}$ (no. 2), a = 13.256(4), b = 13.735(4), c = 17.298(5) Å, α = 94.48(1), β = 94.62(1), γ = 101.60(1)°, V = 3060.7(16) Å^3, Z = 2, μ = 0.06 mm^{-1}, T = 120(2) K, APEX CCD area detector, Mo-K$_\alpha$ radiation, λ = 0.71073 Å, 32 023 reflections (14 008 independent, R_{int} = 0.075), SHELXTL software, least-squares refinement against F^2, final R = 0.062 [7596 reflections with $F^2 > 2\sigma(F^2)$], $R(F^2)$ = 0.175 (all data). The acetone and hexane molecules of crystallisation are highly disordered. CCDC 226864. See http://www.rsc.org/suppdata/cc/b3/b316250h/ for crystallographic data in CIF or other electronic format.

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