ChemComm

This article is part of the

Frontiers in Molecular Main Group Chemistry

web themed issue

Guest editors: Manfred Scheer and Richard Layfield

All articles in this issue will be gathered together online at
www.rsc.org/cc/maingroup

ChemComm

Dynamic Article Links

Cite this: *Chem. Commun.*, 2012, **48**, 5769–5771

www.rsc.org/chemcomm

COMMUNICATION

Alkali-metal mediated reactivity of a diaminobromoborane: mono- and bis-borylation of naphthalene *versus* boryl lithium or hydroborane formation†‡

Sarah Robinson, Jonathan McMaster, William Lewis, Alexander J. Blake and Stephen T. Liddle*

Received 9th March 2012, Accepted 2nd April 2012
DOI: 10.1039/c2cc31758c

Reaction of lithium with PDABBr [PDA = C_6H_4-1,2-$(NTripp)_2$, Tripp = 2,4,6-$Pr^i_3C_6H_2$] and naphthalene afforded 2- and 2,6-borylated naphthalenes; conversely, use of high-sodium lithium (0.5% Na) afforded the lithium boryl [(PDAB)Li$(THF)_2$]; this work establishes that main group reagents can achieve selective borylations of fused polycyclic aromatics under mild conditions in good yields.

The direct and selective functionalisation of hydrocarbon C–H bonds is an enduring challenge in synthetic chemistry.[1] Significant progress has been made in the conversion of aliphatic C–H bonds into C–C, C=C, and C–O bonds and aromatic C–H bonds into C–X bonds (X = C, N, O, halide).[2] In contrast, however, although C–B bonds are rendered highly attractive by virtue of their extensive utility in synthesis, only since 1993 has their metal catalysed preparation from C–H groups been developed.[3] A number of transition metal boryl compounds are active in borylation chemistry, but arguably iridium complexes are the most effective. For example, Marder showed that a mixture of [{Ir(OMe)(COD)}$_2$], 4,4′-di-*tert*-butyl-2,2′-bipyridine, and $(Bpin)_2$ (pin = $OCMe_2CMe_2O$) could borylate naphthalene, pyrene, and perylene.[4] For naphthalene, which represents the simplest and most important fused-ring aromatic hydrocarbon, mono- and bis-borylation at the 2- and 2,6- and 2,7-positions, respectively, was observed. This is notable because electrophilic functionalisation at the 1- and 2-positions of naphthalene can be kinetically or thermodynamically controlled, respectively,[5] but regioselective functionalisation is difficult to achieve without directing groups or high-steric loadings.[6]

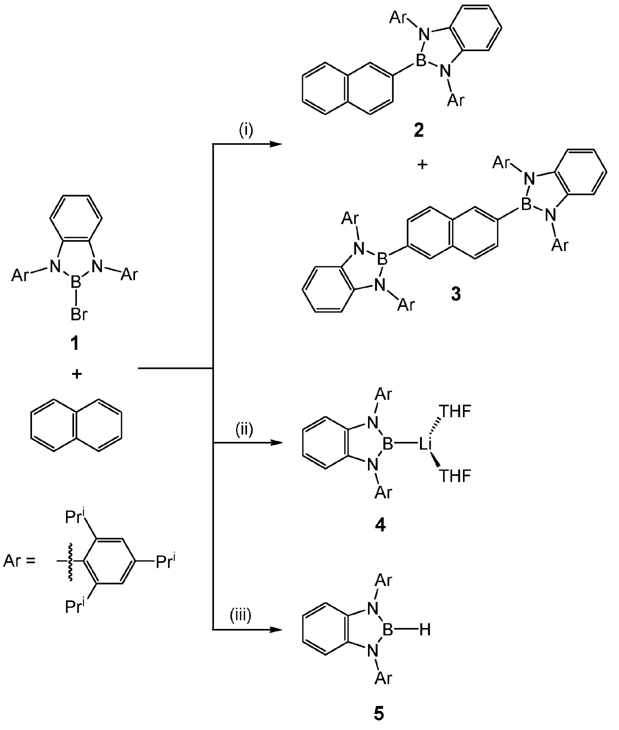
Harsh reaction conditions are often required to effect transition metal-mediated borylations,[3] and some metal catalysts are expensive,[7] which has led to the search for complementary stoichiometric main group reagents that will provide new synthetic methods.[3a] Of pertinence to this point is the report by Mulvey of alkali metal-mediated 2- and 2,6-zincation of naphthalene which could easily be converted into boryl derivatives, although elevated temperatures were required to effect double metallation.[8] Thus, the selective functionalisation and borylation of polycyclic aromatic hydrocarbons under mild conditions represents a significant synthetic hurdle to overcome without invoking the use of expensive metal complexes. Herein, we report our preliminary results in this area, namely the controllable switching of the reactivity of a sterically demanding diaminobromoborane in one pot to afford mono- (2-borylated) and bis- (2,6-diborylated) naphthalenes, or a boryl lithium, or a hydroborane. The reactivity is completely controlled by the nature of the alkali metal and the regioselective borylated products are notable for establishing the formation of thermodynamic, rather than kinetic, isomers under mild reaction conditions.

Treatment of the 1,2-phenylenediamine C_6H_4-1,2-(NH-2,4,6-$Pr^i_3C_6H_2)_2$ (**PDAH$_2$**), which has been fully characterised and was prepared in 62% yield by a standard palladium-catalysed cross coupling of C_6H_6-1,2-Br_2 and NH_2-2,4,6-$Pr^i_3C_6H_2$,[9] with calcium hydride and boron tribromide afforded, after work-up, multi-gram quantities of PDABBr (**1**) as a cream powder in 44% yield.[10] The characterisation data for **1** fully support its formulation. In particular, the ^{11}B NMR spectrum of **1** exhibits a broad singlet at 24.6 ppm and the X-ray crystal structure reveals a planar, three-coordinate boron which is coordinated to a terminal bromide and the two amine centres of the PDA diamine scaffold. In contrast to boron trihalide compounds, **1** is air- and moisture stable; hexane solutions of **1** left under a static atmosphere of air are stable indefinitely and **1** is recovered unchanged if a hexane solution of **1** is allowed to evaporate from an open flask. The stability of **1** demonstrates the steric protection afforded to the boron centre and is germane in terms of the ease of use of this compound for synthetic applications. With compound **1** in hand we explored its reactivity with lithium and potassium. We observed dramatically different, and switchable, reactivity which is mediated by the nature of the alkali metal and this is summarised in Scheme 1.

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.
E-mail: stephen.liddle@nottingham.ac.uk; Fax: +44 115 951 3563; Tel: +44 115 846 7167

† This article is part of the *ChemComm* 'Frontiers in Molecular Main Group Chemistry' web themed issue.

‡ Electronic supplementary information (ESI) available: Full experimental, crystallographic, and computational details for **1–5**. CCDC 862667–862671. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc31758c



Scheme 1 Synthesis of **2–5**. Reagents and conditions: (i) lithium powder, THF, −10 °C, 6 h, –LiBr; (ii) high-sodium content lithium powder (0.5% Na), THF, −10 °C, 6 h, –LiBr; (iii) potassium, DME, −78 or −10 °C or room temperature, –KBr.

Carried out under mild conditions (−10 °C, 6 h), the reaction of lithium powder with naphthalene and **1** in a 1 : 1 ratio under argon afforded a mixture of (PDAB)-2-$C_{10}H_7$ (**2**) and (PDAB)$_2$-2,6-$C_{10}H_6$ (**3**). Compounds **2** and **3** are easily separated by fractional crystallisation and were isolated as colourless crystals in average yields of 46 and 34%, respectively.[10] When the reaction under these conditions is carried out in a 1 : 2 ratio **3** is isolated in high yield (82% av.) yield with only trace (4–6%) amounts of **2** formed. The ^{1}H NMR spectrum of **2** exhibits four broad multiplets (2 : 3 : 1 : 1 ratio) attributable to naphthalene protons. The ^{13}C NMR spectrum of **2** exhibits ten naphthalene carbon resonances. Together these data are indicative of the now asymmetric mono-borylated naphthalene unit. The ^{11}B NMR resonance at 27.3 ppm is shifted only slightly compared to **1** and is consistent with retention of a trigonal planar boron centre in **2**. For symmetric **3**, the ^{1}H NMR spectrum reveals only three naphthalene resonances and the ^{11}B NMR spectrum shows a singlet at 25.8 ppm. The NMR data support the 2-borylated and 2,6-diborylated assignments for **2** and **3** and this was confirmed by X-ray crystallographic studies (Fig. 1).

The 2- and 2,6-regioselectivity observed in **2** and **3** is noteworthy. The thermodynamic (2,6) and not the kinetic (1,5) positions are functionalised even though the reaction is carried out under mild conditions which favour kinetic products and this is likely due to the steric demands of the PDA group. The crystalline yield of 46% for **2** is comparable to a 49% yield for the iridium catalysed preparation of 2-(Bpin)$C_{10}H_7$.[4] Furthermore, the second borylation step could occur at the 6- or 7-positions after the initial 2-borylation and this was observed in the iridium catalysed synthesis of (Bpin)$_2C_{10}H_6$ where formation of the 2,6- and 2,7-isomers was observed in essentially equal quantities.[4] However, by using **1** the formation of the 2,7-isomer of **3** is completely suppressed and the crystalline yield of 34% for **3** compares well to yields of 10 and 12% for 2,6- and 2,7-(Bpin)$_2C_{10}H_6$. Finally, **3** can be isolated in good yield by adjusting the reaction stoichiometry and the bulky PDA group imparts crystallinity enabling straightforward separation of **2** and **3**.

The structures of **2** and **3** were determined by X-ray diffraction and are illustrated in Fig. 1.[10] The structural data confirm the mono- and bis-borylations of naphthalene and **3** straddles an inversion centre commensurate with its 2,6-functionalisation. Interestingly, in both **2** and **3** the naphthalene ring is coplanar with respect to the PDAB ring suggesting some conjugation between the formally vacant 2p-orbital on boron and the filled carbon 2p-orbital of the *ipso*-carbon(s) of the naphthalene rings. Additionally, in **2** and **3** the 1,3-hydrogens (and symmetry-related 5,7-hydrogens for **3**) are aligned towards the centroids of the Tripp rings with distances of 2.63 and 2.81 Å and 2.79 and 2.91 Å, respectively, which may provide a further stabilising contribution towards the co-planar arrangements. The B–N and B–C distances for **2** and **3** are unexceptional.[11]

The assembly of **2** and **3** from relatively simple main group reagents raises the question as to the reaction mechanism. Clearly the steric demands of **1** play a part, but the role of the lithium in this reaction is intriguing. Unfortunately, we were not able to definitively establish the fate of the eliminated hydrogen atoms.[12] However, lithium bromide was eliminated which suggests that HBr elimination is unlikely. We tentatively suggest that the lithium reduces the naphthalene ring and eliminates lithium bromide; the resulting PDAB$^+$ cation could then electrophilically attack the electron rich naphthanalide ring, which is then poised to eject H$^\bullet$, ultimately forming dihydrogen before further reduction occurs. Such an electrophilic attack would be notable as, in contrast to Friedel Crafts chemistry, intermolecular arene borylation by electrophilic substitution is rare and ether cleavage-side reactions, which are not observed with **1**, are common with strong boron electrophiles.[7,13] Although the formation of PDAB$^+$ under reducing conditions may seem counterintuitive, the reduction is clearly slow (see below). Where radical or borylene groups are generated in the presence of naphthalene either no reaction occurs, the boron centres insert into C–H bonds (rather than substituting them), or [2 + 1] cycloaddition reactions are observed.[14,15] Thus the reductive reactivity of **1** adds to a complex palate of reactivity which is emerging in boryl/borylenoid chemistry. The experimental observation of emerald green solutions is consistent with the formation of the naphthanalide radical anion, but given that a radical is converted to a diamagnetic compound little could be gleaned from solution studies. This reactivity suggests that the electron transfer could be relatively slow with pure lithium, thus enabling the formation of **2** and **3** instead of a boryl lithium complex of which there are only a small number.[16] In order to test our hypothesis we reacted **1** with *high*-sodium lithium powder (0.5% Na) as this is a more reactive source of lithium than pure lithium.

Accordingly, treatment of **1** with high-sodium lithium under essentially identical reaction conditions to that which produced **2** and **3** afforded, after work-up, colourless crystals of the new boryl lithium complex [(PDAB)Li(THF)$_2$] (**4**)

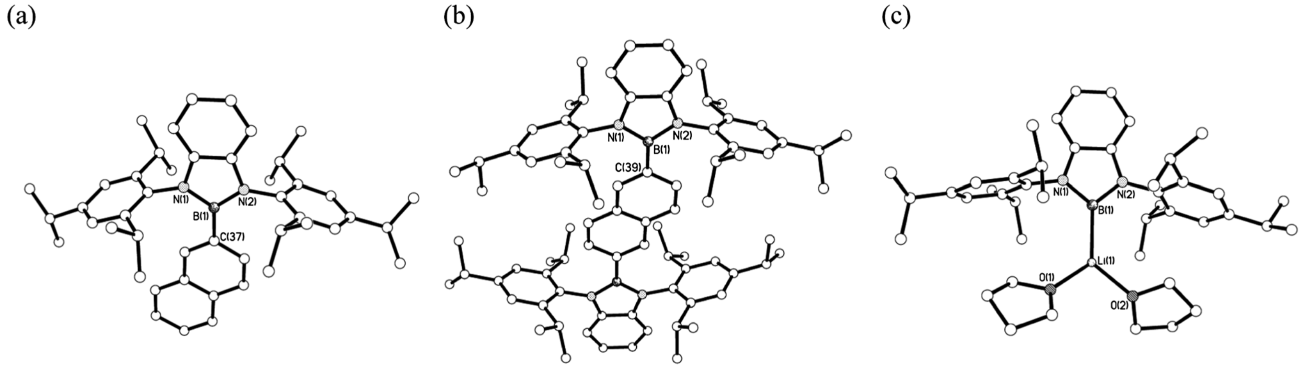


Fig. 1 Molecular structures of (a) **2**, (b) **3**, and (c) **4** with selective atom labelling and hydrogen atoms omitted for clarity. Selected bond lengths (Å): (a) B(1)–C(37) 1.581(3), B(1)–N(1) 1.441(3), B(1)–N(2) 1.438(3); (b) B(1)–C(39) 1.573(4), B(1)–N(1) 1.443(4), B(1)–N(2) 1.441(4); (c) B(1)–Li(1) 2.285(4), B(1)–N(1) 1.483(3), B(1)–N(2) 1.482(3), Li(1)–O(1) 1.919(4), Li(1)–O(2) 1.952(4).

in 85% (av.) yield. The spectroscopic and analytical data for **4** are consistent with its formulation and the ^{11}B and ^{7}Li NMR spectra reveal broad singlets at 51.0 and 0.6 ppm, respectively.[10] The crystal structure of **4** is shown in Fig. 1 and reveals a trigonal planar lithium centre coordinated by two THF molecules and the boryl PDAB ligand. The B–Li bond length was found to be 2.285(4) Å which falls in the range of known B–Li bond distances.[16]

The combined yield of **2** and **3** from the lithium reaction is 80% and the high-sodium lithium reaction produces **4** in 85% yield. The switchable nature of this reaction is therefore clear-cut, clearly mediated by the nature of the lithium metal employed, and entirely controllable. To further confirm this we reacted **1** with the more reactive alkali metal potassium and isolated the hydroborane compound PDABH (**5**) with an average yield of 82%.[10] Presumably a boryl potassium complex is formed transiently, but the putative B–K bond, which would be expected to be more ionic than the B–Li bond in **4**, must be too reactive and thus abstracts a proton from solvent to give **5**.

To summarise, this study establishes that alkali metals can be employed to modulate the reactivity of a diaminobromoborane. On one hand regioselective mono- and bis-borylation of naphthalene can be effected, or alternatively boryl lithium or hydroborane compounds can be prepared.

We thank the Royal Society, EPSRC, ERC, and the University of Nottingham for generously supporting this work.

Notes and references

1 *Activation and Functionalisation of C–H Bonds*, ed. K. L. Goldberg and A. S. Goldman, ACS Symposium Series, American Chemical Society, Washington DC, 2004, vol. 885.

2 Selected reviews: (*a*) J. A. Labinger and J. E. Bercaw, *Top. Curr. Chem.*, 2011, **35**, 29; (*b*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (*c*) M. T. Whited and R. H. Grubbs, *Acc. Chem. Res.*, 2009, **42**, 1607; (*d*) R. E. Mulvey, *Acc. Chem. Res.*, 2009, **42**, 743; (*e*) J. F. Hartwig, *Nature*, 2008, **455**, 314; (*f*) R. N. Perutz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2007, **46**, 2578; (*g*) K. R. Campos, *Chem. Soc. Rev.*, 2007, **36**, 1069; (*h*) M. Lersch and M. Tilset, *Chem. Rev.*, 2005, **105**, 2471; (*i*) R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, 2001, 2437; (*j*) Y. Guari, S. Sabo-Etienne and B. Chaudret, *Eur. J. Inorg. Chem.*, 1999, 1047.

3 (*a*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890; (*b*) J. F. Hartwig, *Chem. Soc. Rev.*, 2011, **40**, 1992.

4 D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder and R. N. Perutz, *Chem. Commun.*, 2005, 2172.

5 L. D. Field, S. Sternhell and H. V. Wilton, *J. Chem. Educ.*, 1999, **76**, 1246.

6 T. Ishiyama and N. Miyaura, *Chem. Rec.*, 2004, **3**, 271.

7 (*a*) A. DelGrosso, P. J. Singleton, C. A. Muryn and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2011, **50**, 2102; (*b*) A. Del Grosso, M. D. Helm, S. A. Solomon, D. Caras-Quintero and M. J. Ingelson, *Chem. Commun.*, 2011, **47**, 12459.

8 W. Clegg, S. H. Dale, E. Hevia, L. M. Hogg, G. W. Honeyman, R. E. Mulvey and C. T. O'Hara, *Angew. Chem., Int. Ed.*, 2006, **45**, 6548.

9 (*a*) T. Wenderski, K. M. Light, D. Ogrin, S. G. Bott and C. J. Harlan, *Tetrahedron Lett.*, 2004, **45**, 6851; (*b*) J.-Y. Liu, Y. Zheng, Y.-G. Li, L. Pan, Y.-S. Li and N.-H. Hu, *J. Organomet. Chem.*, 2005, **690**, 1233.

10 See the Supporting Information‡ for full details.

11 From a search of the Cambridge Structural Database (CSD v1.13, date: 15/12/2011): F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.

12 Attempts to trap the headspace of the reactions or to analyse the LiBr byproduct for LiH proved inconclusive.

13 (*a*) E. L. Muetterties, *J. Am. Chem. Soc.*, 1960, **82**, 4163; (*b*) E. L. Muetterties and F. N. Tebbe, *Inorg. Chem.*, 1968, **7**, 2663; (*c*) A. Del Grosso, C. A. Muryn, R. G. Pritchard and M. J. Ingleson, *Organometallics*, 2010, **29**, 241; (*d*) V. I. Bregadze, I. D. Kosenko, I. A. Lobanova, Z. A. Starikova, I. A. Godovikov and I. B. Sivaev, *Organometallics*, 2010, **29**, 5366.

14 (*a*) P. Bissinger, H. Braunschweig, K. Kraft and T. Kupfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 4704; (*b*) P. Bissinger, H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kupfer, K. Radacki and K. Wagner, *J. Am. Chem. Soc.*, 2011, **133**, 19044; (*c*) D. P. Curran, A. Boussonnière, S. J. Geib and E. Lacôte, *Angew. Chem., Int. Ed.*, 2012, **51**, 1602.

15 The reactivity of **1** contrasts to less sterically demanding diamino-haloboranes which react with alkali metals to afford diborane(4) compounds, see: L. Weber, H. B. Wartig, H.-G. Stammler and B. Neumann, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2663.

16 (*a*) Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113; (*b*) Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2007, **46**, 6710; (*c*) M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570; (*d*) Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069.