Intramolecular borylation reaction catalyzed by Lewis acid: preparation of 1*H*-2,1-benzazaborole derivatives

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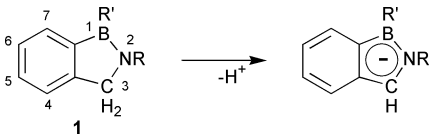
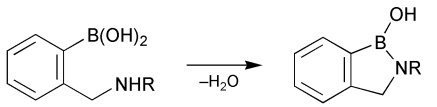
It has been found that 1*H*-2,1-benzazaboroles can be prepared by the interaction of substituted benzylaminochloroboranes with Al_2Cl_6 in CH_2Cl_2 at 0 °C, the ^{13}C NMR spectroscopy data obtained being in favour of an electrophilic substitution mechanism involving formation of cationic complexes as reactive intermediates.

The π-delocalized anions accessible through deprotonation of 1*H*-2,1-benzazaboroles (**1**) are isoelectronic with indenyl anions (Scheme 1), making them attractive precursors for single site olefin polymerization catalysts based on heterocyclic analogues of metallocenes[1] (*cf.* ref. 2).

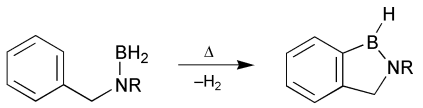


Scheme 1

The two well known approaches towards benzazaborole derivatives involve intramolecular condensation of *o*-(aminomethyl)benzene boronic acids[3] (Scheme 2) and intramolecular cyclization of benzylaminoboranes[4] (Scheme 3). The first method is applicable for preparation of derivatives with B–OH or B–O–B fragments only, while the second route requires high process temperatures and is not applicable to compounds in which there is no B–H bond.

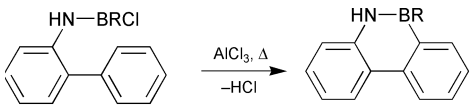


Scheme 2

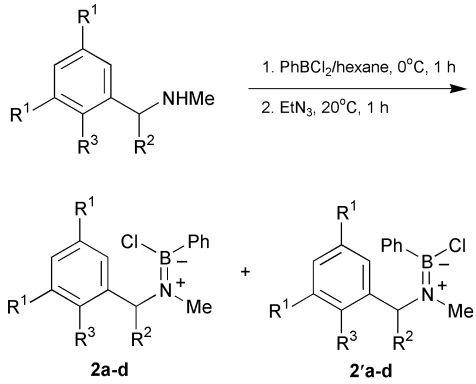


Scheme 3

As part of our program to develop synthetically attractive approaches towards precursors for heterocyclic analogues of cyclopentadienyl ligands, we studied the utility of Lewis acid catalysed borylation reactions for the preparation of benzoborazoles **1**. To the best of our knowledge there have been no data on their preparation by this reaction, the closest related data being those of M. J. S. Dewar on the $AlCl_3$ catalysed preparation of (10*R*)-9-aza-10-boraphenanthrene and related heteroaromatics at high temperature and without solvent[5] (Scheme 4).



Scheme 4

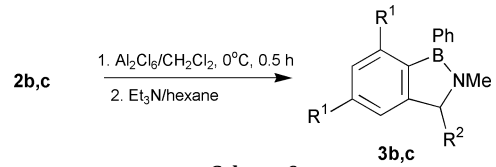


Scheme 5

The starting materials, halogen substituted aminoboranes **2a**–**d**,† have been prepared by the procedures analogous to those described in refs. 6 and 7 (Scheme 5). There are two sets of signals in the ^1H and ^{13}C NMR spectra of each of these compounds indicating the presence of mixtures of *cis*- and *trans*-isomers, obviously due to partially double bond character of the B–N bond‡ (*cf.* ref. 6).

Aminoboranes **2a** and **2b**, when treated with $AlCl_3$ under Dewar's conditions[5] (without solvent, 150 °C) yielded polymeric products only.

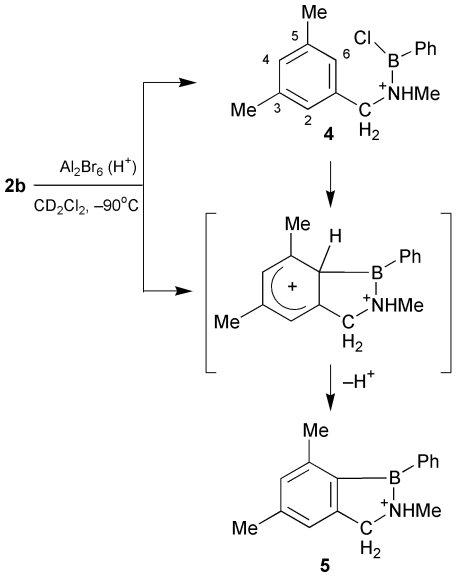
It has been found that the interaction of compounds **2b** and **2c** with equimolar amounts of Al_2Cl_6 in CH_2Cl_2 at 0 °C results in formation of the target products, **3b** and **3c**, respectively, the yields being 75% (Scheme 6).§ In contrast, the compounds **2a** and **2d** do not react at 0 °C, while at rt they give multicomponent mixtures of unidentified products.



Scheme 6

The mechanism of the cyclization reaction has been studied by NMR using **2b** as starting material, CD_2Cl_2 solvent and Al_2Br_6 as a Lewis acid which is more soluble in this solvent than Al_2Cl_6.¶ These experiments indicate that upon the interaction of **2b** with Al_2Br_6 at −90 °C a mixture of **4** and **5** is formed, their ratio being approximately 1:1 (Scheme 7).‖ When the temperature rises to 0 °C, the structure **4** transforms entirely into **5**.

The results reported here suggest that intramolecular electrophilic borylation is a viable approach toward 1*H*-2,1-benzaza-



Scheme 7

boroles, starting from readily available and inexpensive chemicals.

Notes and references

† Satisfactory spectral data have been obtained for all the new compounds. The signals of the carbon atoms bearing B-centred fragments were not observed in the ^{13}C NMR spectra.

‡ For example, the mixture of **2b** and **2b′** (approx. 1 : 1, numeration as for structure **4**): ^1H NMR (CD_2Cl_2) δ 2.35 (s, 6H, 3- and 5-CH_3), 2.37 (s, 6H, 3- and 5-CH_3), 2.99 (s, 3H, N–CH_3), 2.65 (s, 3H, N–CH_3), 4.59 (s, 2H, N–CH_2), 4.40 (s, 2H, N–CH_2), 6.99 (s, 1H, H^4), 6.96 (s, 1H, H^4), 7.01 (s, 2H, H^2 and H^6), 6.88 (s, 2H, H^2 and H^6), 7.3–7.8 (m, 10H, Ph); ^{13}C NMR (CD_2Cl_2) δ 21.28 (q, 2C), 21.30 (q, 2C), 38.0 (q), 37.3 (q), 56.0 (t), 56.4 (t), 125.7 (d, 2C), 125.0 (d, 2C), 127.9 (d, 2C), 127.8 (d, 2C), 129.07 (d), 129.10 (d), 129.28 (d), 129.32 (d), 133.1 (d, 2C), 132.5 (d, 2C), 138.12 (s), 138.14 (s), 138.3 (s, 2C), 138.4 (s, 2C).

§ Preparation of **3b**. Chloroaminoborane **2b** (2 mmol) was added to the suspension of Al_2Cl_6 (2 mmol) in 5 mL of CH_2Cl_2 at 0 °C whilst stirring in an argon atmosphere. The dark-red solution formed after stirring for 0.5 h was added dropwise to the solution of 1 mL NEt_3 in 30 mL of hexane at 0 °C. The reaction mixture was allowed to warm to rt, decanted and evaporated. The residue was extracted with 5 mL of hexane, the solution was filtered and evaporated. ^1H NMR (CD_2Cl_2) δ 2.32 (s, 3H, 5- or 7-CH_3), 2.49 (s, 3H, 7- or 5-CH_3), 3.13 (s, 3H, N–CH_3), 4.36 (s, 2H, CH_2), 7.00 (m, 1H, H^4 or H^6), 7.18 (m, 1H, H^6 or H^4), 7.6–7.7 (m, 5H, Ph); ^{13}C NMR (CD_2Cl_2) δ 21.3 (q), 21.6 (q), 34.4 (q), 60.5 (t), 119.9 (d), 127.7 (d, 2C), 127.8 (d), 129.0 (d), 132.6 (d, 2C), 138.7 (s), 141.4 (s), 151.7 (s); ^{11}B NMR (CD_2Cl_2) δ 40.4; MS 235 (M^+). Analogous procedure was used for the preparation of **3c**. ^1H NMR (CD_2Cl_2) δ 3.14 (s, 3H, N–CH_3), 5.44 (s, 1H, CH), 7.28–7.34 (m, 1H), 7.36–7.42 (m, 1H), 7.42–7.55 (m, 5H), 7.60–7.66 (m, 1H), 7.66–7.72 (m, 2H), 7.94–7.99 (m, 1H), 8.00–8.06 (m, 2H); ^{13}C NMR (CD_2Cl_2) δ 32.6 (q), 74.9 (d), 122.9 (d), 126.8 (d), 127.8 (d, 2C), 127.9 (d), 128.2 (d, 2C), 129.00 (d, 2C), 129.03 (d), 129.1 (d), 130.7 (d), 133.9 (d, 2C), 140.4 (s), 155.7 (s); ^{11}B NMR (CD_2Cl_2) δ 40.4; MS 283 (M^+).

¶ Taking into account that $AlCl_3$ used in the preparative experiments obviously contains some proton donating impurities ($AlCl_2OH$ and the like) we did not use 'extra dry' Al_2Br_6 in mechanistic experiments.

‖ Structure **4**: ^1H NMR (−15 °C, CD_2Cl_2) δ 2.25 (s, 6H, 3- and 5-CH_3), 3.45 (d, J_{HNCH} 5 Hz, 3H, N–CH_3), 4.69 and 4.73 (m, J_{HCH} 13, J_{HNCH} 8 and 4 Hz, 2H, N–CH_2), 7.04 (br s, 1H, N–H), 7.00 (s, 1H, H^4), 7.08 (s, 2H, H^2 and H^6), 7.5–8.0 (m, 5H, Ph); ^{13}C NMR (−42 °C, CD_2Cl_2) δ 20.8 (q, 2C), 39.6 (q), 60.5 (t), 126.7 (s), 127.6 (d, 2C), 129.1 (d, 2C), 132.6 (d), 137.0 (d, 2C), 138.8 (d), 139.9 (s, 2C). Structure **5**: ^1H NMR (−15 °C, CD_2Cl_2) δ 2.53 (s, 3H, 5- or 7-CH_3), 2.60 (s, 3H, 7- or 5-CH_3), 3.11 (d, J_{HNCH} 6 Hz, 3H, N–CH_3), 4.55 (dd, J_{HCH} 16, J_{HNCH} 2 Hz, 1H, N–CH_2), 5.32 (dd, J_{HCH} 16 Hz, J_{HNCH} 6 Hz, 1H, N–CH_2), 6.80 (br s, N–H), 7.28 (s, 1H, H^4 or H^6), 7.29 (s, 1H, H^6 or H^4), 7.5–8.0 (m, 5H, Ph); ^{13}C NMR (−42 °C, CD_2Cl_2) δ 22.3 (q), 22.5 (q), 40.9 (q), 60.4 (t), 121.5 (d), 128.7 (d, 2C), 132.5 (d), 133.8 (d), 134.5 (d, 2C), 148.7 (s), 151.6 (s), 154.1 (s).

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