# Communications

Borylation

A Boronium Ion with Exceptional Electrophilicity**

*Aleksandrs Prokofjevs, Jeff W. Kampf, and Edwin Vedejs**

During our studies on aromatic borylation,[1] we considered the combination of a highly electrophilic R_2BNTf_2 reagent with a base that would neutralize the $HNTf_2$ by-product of borylation without deactivating the electrophile. In principle, these requirements might be satisfied by 1,8-bis(dimethylamino)naphthalene (**1**, Scheme 1), a hindered and exceptionally basic aniline that finds numerous applications as a basic
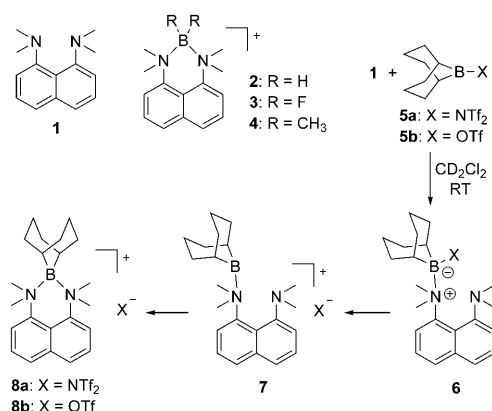
Scheme 1.

catalyst or reagent due to its legendary lack of nucleophilicity.[2,3] Strong electrophiles interact weakly, if at all, with the amine nitrogen atoms, and very few examples are known in which stable bonds to nitrogen can be formed between **1** and electrophilic groups larger than hydrogen.[2,4–7] Among these exceptional cases, cyclic boronium structures **2** and **3** are relatively stable because the subunits BH_2 and BF_2 have minimal steric requirements.[5] However, the more hindered BMe_2 derivative **4** has not been detected and no analogous BR_2 structures are known.[5a,8] In view of this long history, we were somewhat surprised to find that an adduct is readily formed simply on mixing **1** with 9-borabicyclo[3.3.1]nonane (9-BBN) bis-triflimide reagent **5a**, despite the transannular steric demands of the 9-BBN core and the need to form adjacent quaternary bonds to the boron and nitrogen atoms.[9,10] The remarkable structural features and unusual reactivity of this adduct are the subject of the following communication.

[*] A. Prokofjevs, Dr. J. W. Kampf, Prof. Dr. E. Vedejs
    Department of Chemistry, University of Michigan
    930 N. University Ave, Ann Arbor, MI 48109-1055 (USA)
    Fax: (+1) 734-615-1628
    E-mail: edved@umich.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005663.

The previously unreported **5a** was easily prepared from the commercially available 9-BBN dimer and bis(trifluoromethanesulfonyl)imide by heating in toluene. Combination of the bulky boron reagent **5a** with a stoichiometric amount of **1** in CD_2Cl_2 at room temperature formed a deep-red solution that turned colorless within seconds of mixing the reagents. Analysis of the resulting solution by ^{11}B NMR spectroscopy revealed a signal at $\delta = 16.2$ ppm, suggesting that a single tetracoordinate[11] boron atom is present in the product. The ^{19}F NMR spectrum showed a single peak at $\delta = -79.4$ ppm, which is characteristic of bis-triflimide anion,[12] so the boron-containing fragment was thus identified to be a cation. The ^1H NMR spectrum suggested that the solution structure of the cation is highly symmetrical on the NMR timescale at room temperature. Only four groups of protons corresponding to the diamine subunit **1** were observed, including one sharp singlet for all four methyl groups, and a well-resolved (at 500 MHz) AMX system for the aromatic protons. Other peaks in the ^1H and ^{13}C NMR spectra were also consistent with a symmetrical time-averaged structure for the cation (e.g., a single ^{13}C methyl peak at $\delta = 57.1$ ppm, and only three peaks for the 9-BBN cage carbon atoms). Since the covalent adduct **6** ($X = NTf_2$) is ruled out by observation of the bis-triflimide anion,[12b] and the tricoordinate cationic borenium structure **7** ($X = NTf_2$) is not consistent with the observed ^{11}B NMR chemical shift, the most plausible structure for the species formed from **1** and **5a** is the exceptionally hindered boronium salt **8a**. Formation of **8a** may follow the logical sequence in Scheme 1, but alternative mechanisms have not been excluded.[13] Formation of **8a** in greater than 95% yield depends on the low nucleophilicity of the counterion, and only partial conversion into the boronium ion was observed when **5b** was used instead of **5a**. Thus, when equimolar **1** and the triflate reagent **5b** were mixed in CD_2Cl_2, the resulting solution showed both starting **1** and product **8b** (ca. 1.2:1 ratio by ^1H NMR assay).

The low temperature ^1H NMR behavior of **8a** in CD_2Cl_2 is complex and indicates the presence of unsymmetrical species. Decreasing the temperature broadens the ^1H NMR singlet corresponding to the *N*-methyl groups, until it turns into a broad set of at least three maxima that are not fully resolved even at $-80\,°C$. Additional information about the solution structure is provided by the very different shielding of the two bridgehead hydrogen atoms of the 9-BBN cage observed in the low-temperature ^1H NMR spectra. While the spectrum at room temperature shows only one peak for both bridgehead protons, two distinct resonances are observed at $-80\,°C$. One of the bridgehead hydrogen atoms gives rise to a peak at an unremarkable $\delta = 1.57$ ppm, while the other appears at $\delta = 0.33$ ppm. Such prominent shielding by the aromatic ring is consistent with the 9-BBN cage being tilted toward one side
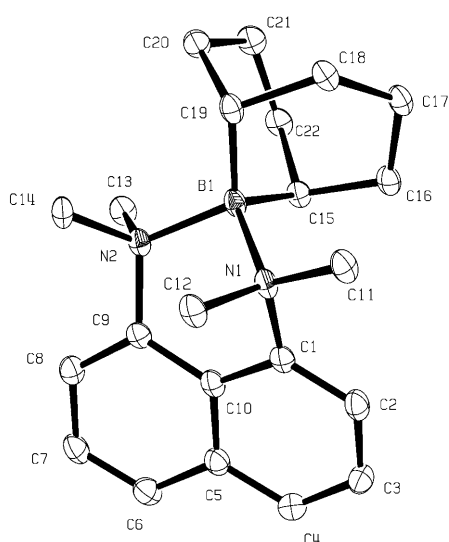
Figure 1. ORTEP of **8a** (50% probability thermal ellipsoids). The counterion and hydrogen atoms are omitted for clarity.

of the naphthalene plane to place the shielded proton above the aromatic π-system.

Slowly cooling a solution of **8a** in CH$_2$Cl$_2$/hexanes produced large platelike crystals, suitable for X-ray diffraction studies.[14] Due to strain imposed by the hindered environment, the structure of **8a** (Figure 1) is unsymmetrical, the B−N bonds are very long, and both the 9-BBN cage and the bis(dimethylamino)naphthalene unit are severely twisted. While the C15-B1-C19 angle (106°) and C−B bond lengths (B1−C15 1.63, B1−C19 1.61 Å) are within the expected range for 9-BBN derivatives,[9a, 15] the C20-C19-C15-C22 and C18-C19-C15-C16 dihedral angles are in excess of 10°. Furthermore, strong distortion of the diamine base is evidenced by the N2-C9-C1-N1 dihedral angle of 28.9°, compared to 20.3° in **1**.[16] On the other hand, the aniline N···N distance in **8a** (2.65 Å) is substantially shorter than that reported for **1** (2.79 Å), and only slightly exceeds that in salts of protonated **1**, such as the sulfonimide salt **1**·HNMs$_2$ (2.60 Å).[17]

The arrangement of the 9-BBN cage in crystals of **8a** is also noteworthy. The bridgehead carbon atoms C15 and C19 are quite distinct, and C15 is pseudo-axial with respect to the distorted half-chair boron heterocycle. This places C15H above the aromatic π system, consistent with the low-temperature ^{1}H NMR result indicating substantial shielding of one of the bridgehead protons. Another prominent structural detail is the length of the B−N bonds (B1−N1 1.72, B1−N2 1.73 Å), compared to values of 1.58–1.60 Å in simpler boronium cations such as [H$_2$B(NMe$_3$)(MeIm)]$^+$ or [H$_2$B(NH$_2$Me)-(MeIm)]$^+$ (MeIm = 1-methylimidazole).[18,19] Since the distance of 1.72–1.73 Å greatly exceeds the sum of the covalent radii for B and N atoms (1.55 Å),[20] the calculated Pauling bond order for both B−N bonds in **8a** is only about 0.55.[21]

The unusual structural features prompted computational modeling of cation **8a**.[22a] Gas-phase geometry optimization at the M06-2X/6-31G(d,p) level produced a structure that is in close agreement with the X-ray data (e.g., B−N bond lengths are within 0.01 Å of the experimental values).[22b] An NBO

analysis[22c] performed on the optimized structure indicates that the boron atom carries the bulk of the positive charge (NBO charge 0.97), and Wiberg bond orders of the two B−N bonds are 0.52 and 0.53.

It was also of interest to compare the interactions of other amines with the potent Lewis acid **5a** in solution. When triethylamine was combined with **5a** in CD$_2$Cl$_2$, clean formation of borenium ion **10** was observed (Scheme 2). No evidence for boronium structure **11** was detected, even when excess triethylamine was used. The borenium character of **10**
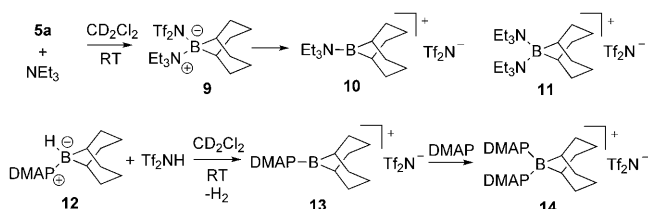
Scheme 2.

is substantiated by a strongly deshielded ^{11}B NMR peak at δ = 85.1 ppm, as well as the bis-triflimide anion peak at δ = −79.5 ppm in the ^{19}F NMR spectrum,[12a] evidence that rules out alternative structure **9**. For simplicity, **9** is tentatively shown as a precursor of **10**, although direct conversion from **5a** is not ruled out.

In contrast to triethylamine, 4-(dimethylamino)pyridine (DMAP) reacted with a stoichiometric amount of **5a** to afford mostly the isolable boronium cation **14** according to the ^{11}B NMR shift of δ = 3.0 ppm (CD$_2$Cl$_2$, RT) along with traces of borenium cation **13** (δ = 66.5 ppm).[23] A much better way to generate **13** in situ was to protonate amine–borane complex **12** with Tf$_2$NH. This method confirmed the chemical shift of **13** and afforded solutions also containing relatively minor amounts of boronium salt **14** (ca. 7–11:1 **13**:**14**). However, the more hindered 2,6-di-*tert*-butyl-4-methylpyridine did not interact with **5a** at room temperature according to ^{1}H and ^{11}B NMR assay.

The most remarkable feature of borenium salt **10** is the absence of any stabilizing π-donor or n-donor substituents at boron, in contrast to **13** and all previously reported persistent borenium ions generated in the condensed phase.[24,25] Comparison of ^{11}B NMR shifts for **10** (δ = 85.1 ppm) and **13** (δ = 66.5 ppm) indicates extensive cation stabilization by π delocalization between DMAP and the boron atom. Other π-stabilized borenium cations have been observed in the ^{11}B chemical shift range of δ = 58.2 to 66 ppm,[1,24,25] and this suggests that **10** may be an exceptionally electrophilic member of the borenium family.

High electrophilicity of boron cations is crucial for potential applications in electrophilic aromatic borylation.[1,26] Thus, different combinations of bis-triflimide **5a** with basic amines generated reagents that react with electron-rich heterocycles to provide *B*-heteroaryl 9-BBN derivatives along with the protonated amines. The reagent consisting of **5a** and the noncomplexing 2,6-di-*tert*-butyl-4-methylpyridine was the most reactive, and borylated *N*-methylindole in seconds at room temperature to afford **16a** (>95% con-

version by NMR spectroscopy), while the cationic reagents **8a** and **10** required several hours at 50°C for similar conversion. No added base was needed with **8a** or **10** because both reagents already contain a "built-in" base (proton sponge **1** and triethylamine, respectively) to neutralize the HNTf$_2$ that forms during borylation. On the other hand, neither **13** nor **14** reacted with *N*-methylindole under these conditions.[27]

While boronium salt **8a** is less potent than the reagent from **5a** and 2,6-di-*tert*-butyl-4-methylpyridine, **8a** is a far more convenient borylating agent. Practical access to **8a** on gram scale is possible by a one-pot procedure from 9-BBN, **1**, and HNTf$_2$ without having to isolate the highly sensitive **5a** (see Supporting Information). Crystallized **8a** is much easier to handle than **5a**, and even survives up to a month of exposure to dry air (dessicator over Drierite), in contrast to **5a** or **10**. Furthermore, the aromatic borylation products obtained by using **8a** are easy to isolate (Table 1). Crystalline products **16a–d** were obtained in high purity simply by extracting the reaction mixtures with hexanes, in which neither unconverted **8a** nor by-product **1·HNTf$_2$** is soluble, followed by solvent evaporation. This procedure minimizes the risk of competing protodeboronation when using **8a**, but it is not feasible with the reagent from **5a** and 2,6-di-*tert*-butyl-4-methylpyridine due to differences in reagent solubility.

The structures of boranes **16a–d** were established by multinuclear NMR spectroscopy, as well as X-ray crystallography in the case of **16a**.[28] Borylation of *N*-methylindole afforded exclusively the 3-substituted regioisomer, in sharp contrast to the previously reported reaction with B(C$_6$F$_5$)$_3$, which produces the 2-borylated *N*-methylindole.[29] Pyrrole **15c** gave a mixture of mono-borylated regioisomers along with some of the diborylated **16c** when one equivalent of **8a** was used (ca. 80% conversion of **15c**), but two equivalents of the borylating agent cleanly produced diborylated pyrrole **16c**. In the reaction with unsubstituted indole, the known *N*-borylation product was produced first,[30] followed by much slower C3-borylation to afford **16d**.

Table 1: Borylation of nitrogen heterocycles with **8a**.[a]

Het-H + **8a** $\xrightarrow[50\,°C]{CH_2Cl_2}$ Het-BBN + **1·HNTf$_2$**

Het-H	Product, Het-BBN	t	Yield [%]
15a	**16a**	1.5 h	96
15b	**16b**	1.5 h	98
15c	**16c**	3.5 h	97[b]
15d	**16d**	5.5 d	97[b]

[a] 1.05 equiv of **8a**, CH$_2$Cl$_2$, 50°C. [b] 2.10 equiv of **8a**.

Several reactions of **8a** suggest that it is in equilibrium with the starting **1** and **5a**. Thus, equimolar **8a** and Tf$_2$NH produced the protonated diamine (**1·HNTf$_2$**) and released **5a** (NMR assay). Furthermore, reaction of **8a** with triethylammonium bis-triflimidate (Et$_3$NH$^+$Tf$_2$N$^-$) yielded **1·HNTf$_2$** and tricoordinate cation **10**, which represents an unusual route from boronium to borenium ions involving formal migration of the 9-BBN fragment to a different amine. These events can be understood if dissociation of **8a** to **1** + **5a** is the first step. The same dissociative mechanism may also help explain the borylations of Table 1, although the identity of the key boron electrophile is not clear. Depending on the timing of bond dissociation and borylation events, a role for tricoordinate borenium ion **7**[1] or even a dicoordinate borinium ion[26a] cannot be ruled out at this point. The equilibrium between **8a** and **1** + **5a** is not directly observable by ^{1}H NMR spectroscopy, but the analogous process does occur in the related system **8b** and **1** + **5b**, containing the more nucleophilic triflate anion (vide supra).

To summarize, covalent boron bis-triflimide **5a** was used to access the unusual boron salts **8a** and **10** by exploiting the excellent leaving-group ability of bis-triflimide anion. The triethylamine-derived **10** expands the range of borenium salts observed in the condensed phase, proving that resonance delocalization of the positive charge is not required for a persistent borenium cation. The hindered boronium salt **8a** cautions against interpreting the name "proton sponge" too literally: in fact, this study proves that **1** can act as a chelating ligand for species much larger than a proton. Also, the unusual structure of **8a** raises a rhetorical question: is there a distinct boundary between the cationic species called "boronium" (tetrasubstituted B), "borenium" (trisubstituted B), and "borinium" (disubstituted B), according to Nöth's terminology?[24] While **8a** should be most appropriately called a boronium salt, the long B−N distances increase the "borinium-like" character, and the unusual reactivity adds a small hint of a borenium ion (**7**). Aside from the structural features of **8a**, the chemoselectivity of its formation also deserves attention. In view of earlier reports that strong electrophiles attack the aromatic system of **1**[3] or abstract hydride from one of the *N*-methyl groups,[3a,31] it is quite intriguing that the reaction between **1** and **5a** proceeds to form **8a**, the most hindered of all plausible products. As evidenced by the electrophilic borylations (Table 1), the steric hindrance of **8a** is responsible for extraordinary reactivity compared to less hindered boronium salts such as **14**.[32,33]

[1] T. S. De Vries, A. Prokofjevs, J. N. Harvey, E. Vedejs, *J. Am. Chem. Soc.* **2009**, *131*, 14679–14687.

[2] R. W. Alder, P. S. Bowman, W. R. S. Steele, D. R. Winterman, *J. Chem. Soc. Chem. Commun.* **1968**, 723–724.

[3] Reviews: a) B. A. Barner, C. A. Faler, M. M. Joullié, *1,8-Bis(dimethylamino)naphthalene. e-EROS Encyclopedia of*

Reagents for Organic Synthesis, DOI 10.1002/047084289X.rb144.pub2, and references therein; b) A. F. Pozharskii, V. A. Ozeryanskii in *The Chemistry of Anilines*, Part 1 (Ed.: Z. Rappoport), Wiley, Chichester, **2007**, pp. 931–1026.

[4] *N*-Monomethylation of 1,8-bis(dimethylamino)naphthalene: R. W. Alder, N. C. Goode, *J. Chem. Soc. Chem. Commun.* **1976**, 108–109.

[5] a) D. D. Axtell, A. C. Cambell, P. C. Keller, J. V. Rund, *J. Coord. Chem.* **1976**, *5*, 129–134; b) T. Onak, H. Rosendo, G. Siwapinyoyos, R. Kubo, L. Liauw, *Inorg. Chem.* **1979**, *18*, 2943–2945; c) P. C. Keller, J. V. Rund, *Inorg. Chem.* **1979**, *18*, 3197–3199; d) J. S. Hartman, J. A. W. Shoemaker, *Polyhedron* **2000**, *19*, 165–176.

[6] Only one transition metal complex of 1,8-bis(dimethylamino)-naphthalene has been structurally characterized: T. Yamasaki, N. Ozaki, Y. Saika, K. Ohta, K. Goboh, F. Nakamura, M. Hashimoto, S. Okeya, *Chem. Lett.* **2004**, *33*, 928–929.

[7] 1,8-Bis(dimethylamino)naphthalene as a proposed ligand for metals: B. L. Lucht, M. P. Bernstein, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1996**, *118*, 10707–10718; F. Farzaneh, M. Majidian, M. Ghandi, *J. Mol. Catal. A* **1999**, *148*, 227–233; J. P. Collman, M. Zhong, C. Zhang, S. Costanzo, *J. Org. Chem.* **2001**, *66*, 7892–7897.

[8] The BCl₂ analog has been claimed, but definitive evidence has not been reported (see ref. [5a]).

[9] For 9-BBN-derived boronium salts containing relatively non-hindered pyridine ligands, see: a) K. Ma, J. W. Bats, M. Wagner, *Acta Crystallogr. Sect. E* **2001**, *57*, o846–o848; b) R. Köster, M. A. Grassberger, *Justus Liebigs Ann. Chem.* **1968**, *719*, 169–186; S. Hünig, I. Wehner, *Heterocycles* **1989**, *28*, 359–363.

[10] Cyclic amino boranes derived from 1,8-diaminonaphthalene and 9-BBN: G. Bar-Haim, M. Kol, *J. Org. Chem.* **1997**, *62*, 6682–6683; G. Bar-Haim, R. Shach, M. Kol, *Chem. Commun.* **1997**, 229–230.

[11] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer, Berlin, **1978**.

[12] a) Tf₂N⁻ salts: R. Arvai, F. Toulgoat, B. R. Langlois, J.-Y. Sanchez, M. Médebielle, *Tetrahedron* **2009**, *65*, 5361–5368; b) A single ¹⁹F peak at δ = −79.8 ppm is observed at −80 °C versus δ = −79.4 ppm at room temperature, typical of the Tf₂N⁻ anion. Covalent bis-triflimide **5a** gives a signal at δ = −70.0 ppm.

[13] Alternatives to consider include an electron-transfer process, a process involving borinium intermediates, or a direct displacement mechanism from **5a** and **1** to **8a** via a transition state that resembles **7**.

[14] a) See Supporting Information for X-ray crystallography details. CCDC 791459 (**8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) The counterion displays a number of close contacts to the cation, the shortest of which is the distance between a bis-triflimide oxygen atom and an *N*-methyl hydrogen atom (2.49 Å).

[15] M. Yalpani, R. Boese, R. Köster, *Chem. Ber.* **1990**, *123*, 1275–1283; C. P. Brock, Y. Fu, K. Niedenzu, H. Nöth, *Main Group Met. Chem.* **1992**, *15*, 53–60; B. Wrackmeyer, B. Schwarze, W. Milius, *J. Organomet. Chem.* **1995**, *489*, 201–205.

[16] H. Einspahr, J.-B. Robert, R. E. Marsh, J. D. Roberts, *Acta Crystallogr. Sect. B* **1973**, *29*, 1611–1617.

[17] D. Henschel, O. Moers, I. Lange, A. Blaschette, P. G. Jones, *Z. Naturforsch. B* **2002**, *57*, 777–790.

[18] P. A. Fox, S. T. Griffin, W. M. Reichert, E. A. Salter, A. B. Smith, M. D. Tickell, B. F. Wicker, E. A. Cioffi, J. H. Davis, Jr., R. D. Rogers, A. Wierzbicki, *Chem. Commun.* **2005**, 3679–3681; M. D. Soutullo, C. I. Odom, A. B. Smith, D. R. McCreary, R. E. Sykora, E. A. Salter, A. Wierzbicki, J. H. Davis, Jr., *Inorg. Chim. Acta* **2007**, *360*, 3099–3102.

[19] A B−N bond length of 1.61 Å has been reported for a 9-BBN-derived boronium ion with bipyridyl as nitrogen ligand (ref. [9a]).

[20] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.

[21] L. Pauling, *J. Am. Chem. Soc.* **1947**, *69*, 542–553.

[22] a) Gaussian 09, Revision A.02 suite of computational programs was used. See the Supporting Information for full details; b) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241; c) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.

[23] C. K. Narula, H. Nöth, *Inorg. Chem.* **1985**, *24*, 2532–2539.

[24] a) W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem.* **2005**, *117*, 5142–5163; *Angew. Chem. Int. Ed.* **2005**, *44*, 5016–5036; b) P. Kölle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399–418.

[25] a) Reports of π-stabilized borenium cations published after ref. [24a]: M. K. Uddin, Y. Nagano, R. Fujiyama, S. Kiyooka, M. Fujio, Y. Tsuno, *Tetrahedron Lett.* **2005**, *46*, 627–630; C. Chiu, F. P. Gabbaï, *Organometallics* **2008**, *27*, 1657–1659; T. Matsumoto, F. P. Gabbaï, *Organometallics* **2009**, *28*, 4252–4253; b) Other recently reported borenium ions: T. Kato, F. S. Tham, P. D. W. Boyd, C. A. Reed, *Heteroat. Chem.* **2006**, *17*, 209–216; C. Bonnier, W. E. Piers, M. Parvez, T. S. Sorensen, *Chem. Commun.* **2008**, 4593–4595; M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303–4305; H. Ott, C. Matthes, A. Ringe, J. Magull, D. Stalke, U. Klingebiel, *Chem. Eur. J.* **2009**, *15*, 4602–4609; see also ref. [26a].

[26] a) A. Del Grosso, R. G. Pritchard, C. A. Muryn, M. J. Ingleson, *Organometallics* **2010**, *29*, 241–249; b) For a review of transition metal catalyzed borylation, see I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931.

[27] The reagent from **5a** + 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) did not borylate toluene or benzofuran at room temperature, but *N*,*N*-diethylaniline reacted slowly with **5a** + DTBMP at room temperature, or with **8a** at 50 °C.

[28] See Supporting Information for X-ray crystallography details. CCDC 791460 (**16a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[29] F. Focante, I. Camurati, D. Nanni, R. Leardini, L. Resconi, *Organometallics* **2004**, *23*, 5135–5141.

[30] B. Wrackmeyer, H. E. Maisel, B. Schwarze, W. Milius, R. Köster, *J. Organomet. Chem.* **1997**, *541*, 97–107; B. Wrackmeyer, B. Schwarze, *J. Organomet. Chem.* **1997**, *534*, 207–211.

[31] Cationic product *i* has been reported from treatment of **1** with the potent electrophile B(C₆F₅)₃: A. Di Saverio, F. Focante, I. Camurati, L. Resconi, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli, A. Sironi, *Inorg. Chem.* **2005**, *44*, 5030–5041.

i
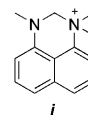
[32] Boronium salt **14** is more stable than **8a**, but more reactive than unhindered analogues (Ref. [24b]): methanolysis of **14** or **8a** occurs with about 90% conversion over about 14 h at 50 °C or 10 min at room temperature, respectively.

[33] After review we learned of related work by A. Del Grosso, P. J. Singleton, C. A. Muryn, M. J. Ingelson, *Angew. Chem.* **2011**, DOI: 10.1002/ange.201006196; *Angew. Chem. Int. Ed.* **2011**, DOI: 10.1002/anie.201006196.