Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

Cite this: *Dalton Trans.*, 2013, **42**, 6417

Reactivity of *C,N*-chelated organoboron compounds with lithium anilides – formation of unexpected 1,2,3-trisubstituted 1*H*-2,1-benzazaboroles†

Martin Hejda,[a] Antonín Lyčka,[b] Roman Jambor,[a] Aleš Růžička[a] and Libor Dostál*[a]

Received 28th November 2012,
Accepted 9th January 2013

DOI: 10.1039/c3dt32850c

www.rsc.org/dalton

A set of *C,N*-intramolecularly coordinated boranes containing various *C,N*-chelating ligands L^{1-3} (where L^1 = [*o*-(CH═N*t*Bu)C_6H_4], L^2 = [*o*-(CH═N-2,6-i$Pr_2C_6H_3$)C_6H_4], L^3 = [*o*-(CH_2NMe_2)C_6H_4]); $L^{1-3}BCl_2$ (for **1** L = L^1, for **2** L = L^2, for **5** L = L^3), L^1BPhCl (**3**) and L^1BCy_2 (**4**) (where Cy = cyclohexyl) were synthesized and fully characterized by multinuclear NMR spectroscopy and in cases of **1** and **3–5** by the single crystal X-ray diffraction analysis. The reaction of **1–3** with the anilides ArNHLi (Ar = 2,6-$Me_2C_6H_3$ or 2,6-i$Pr_2C_6H_3$) proceeded *via* unexpected addition of anilide across the C═N bond yielding 1,2,3-trisubstituted 1*H*-2,1-benzazaboroles **6–11**, whose structures were unambiguously established by single crystal X-ray diffraction analysis (except for **11**) and multinuclear NMR spectroscopy. In contrast, compounds **4** and **5** were inert towards ArNHLi. The investigation dealing with the reaction mechanism between the parent boranes **1–3** and ArNHLi revealed that amidolithiation of the C═N double bond involved in the ligand backbones is the crucial step of the whole reaction. The C═N double bond in **1–3** is activated by its coordination to the *ortho* bonded Lewis acidic boron center, which was also proven by the fact that the non-substituted ligand L^1H did not react with ArNHLi under the same reaction conditions in an analogous reaction.

Introduction

The chemistry of dianionic boraamidinate ligands[1] $[RB(NR')_2]^{2-}$, analogues of popular amidinate ligands[2] $[RC(NR')_2]^-$, has gained considerable attention recently (Fig. 1A). These ligands have been used with success for stabilization of both main group and transition metal compounds.[3] They were also shown to be able to stabilize various radical species.[4] The common feature of all boraamidinate ligands is an application of simple organic groups bonded to the boron atom.[1] As we are interested in the chemistry of *C,N*- or *N,C,N*-chelated main group metal compounds,[5] we decided to try to incorporate a *C,N*-chelating ligand (Fig. 2) into the boron atom in the structure of classical boraamidinates and use such modified ligands for coordination of main group elements (Fig. 1B). The precursors of classical boraamidinates bis(arylamino)boranes may be synthesized by the reaction of $RBCl_2$ with an excess of lithium anilides.[1,3a,4c] By an analogy, we decided to prepare a set of intramolecularly coordinated chloroboranes of the general formula $LBCl_2$ (where L is a *C,N*-chelating ligand) and to treat them with sterically demanding lithium anilides ArNHLi. Surprisingly, these attempts did not lead to formation of desired bis(arylamino)boranes $LB(NHAr)_2$, as precursors for boraamidinate ligands, instead unexpected addition of anilide across the C═N bond took place and a variety of highly substituted 1*H*-2,1-benzazaboroles was isolated in good yields (see further discussion).

Azaboroles represent a class of compounds, which is known in the literature for a long time and can be prepared by a variety of reaction paths.[6] They can also be transformed into an aromatic system and used as ligands for both transition and main group metals as cyclopentadienyl class ligand analogues (Fig. 1C).[6,7] Analogous benzazaboroles, in which the azaborole fragment is fused with an extra aromatic ring, are also known in the literature. These compounds are able to exist in two possible isomeric forms *i.e.* 1*H*-1,2-benzazaboroles (Fig. 1D) and 1*H*-2,1-benzazaboroles (Fig. 1E). The first group of 1*H*-1,2-benzazaboroles has been used, after deprotonation, as ligands for transition metals as analogues of the indenyl anions (Fig. 1D).[8] Reports dealing with substituted 1*H*-2,1-benzazaboroles also appeared in the literature and they were

[a]*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice, Czech Republic. E-mail: libor.dostal@upce.cz; Fax: +420466037068; Tel: +420466037163*

[b]*Research Institute for Organic Syntheses, Rybitví 296, CZ-533 54, Pardubice, Czech Republic*

†Electronic supplementary information (ESI) available: Full assignment of NMR data for **6–11**. CCDC 908864–908873. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32850c

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

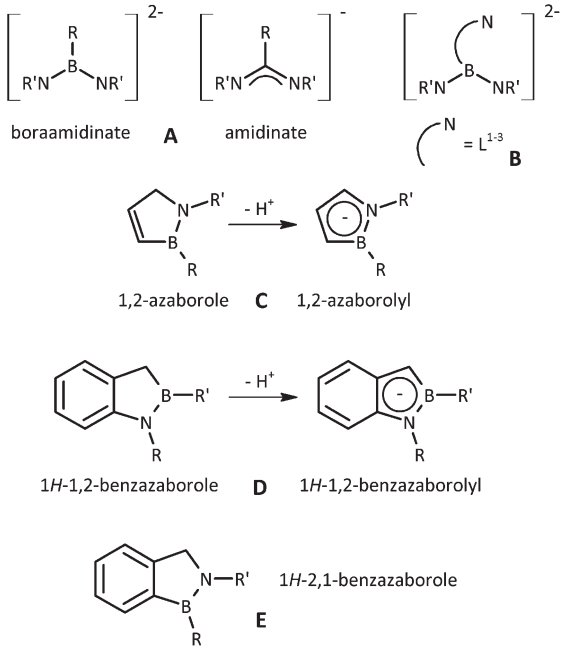


Fig. 1 Structures of known azaboroles and related anions.

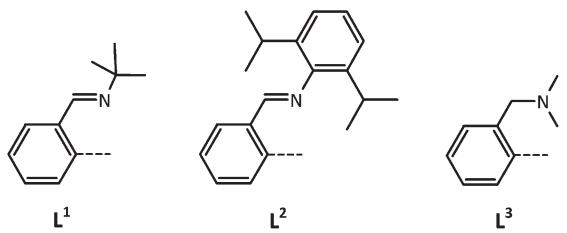


Fig. 2 Structures of the ligands used in this work.

studied due to their antiviral and antibacterial properties.[9] The first examples of 1,2-disubstituted 1*H*-2,1-benzazaboroles were synthesized by Köster *et al*. by condensation reactions of aminoborane adducts at elevated temperatures (~200 °C).[10] In contrast, 1,2,3-trisubstituted 1*H*-2,1-benzazaborole rings are still scarce. These compounds were prepared using intramolecular condensation of *o*-(aminomethyl)benzeneboronic acids.[11] Later on, Nagy *et al.* discovered cyclization of aminoboranes under milder conditions using $AlCl_3$ in dichloromethane at 0 °C.[12] In 2009, Młynarz *et al.* described unexpected formation of 1,2,3-trisubstituted 1*H*-2,1-benzazaborole *via* a reaction of (*N*-benzyl)benzylideneimine-2-boronic acid with diethylphosphite.[13] Recently, several substituted 1*H*-2,1-benzazaboroles have been obtained in the course of the investigation of nitrogen-directed aromatic borylation as well.[14]

Herein, we report on an unexpected procedure for formation of 1,2,3-trisubstituted 1*H*-2,1-benzazaboroles using the reactions of the *C*,*N*-intramolecularly coordinated boranes, containing *C*,*N*-chelating ligands L^{1-3} (where L^1 = [*o*-(CH=N*t*Bu)C_6H_4], L^2 = [*o*-(CH=N-2,6-i$Pr_2C_6H_3$)C_6H_4], L^3 = [*o*-(CH_2NMe_2)C_6H_4], Fig. 2); $L^{1-3}BCl_2$ (for **1** L = L^1, for **2** L = L^2, for **5** L = L^3), L^1BPhCl (**3**) and L^1BCy_2 (**4**) (where Cy = cyclohexyl) with the lithium anilides ArNHLi (Ar = 2,6-$Me_2C_6H_3$, or 2,6-i$Pr_2C_6H_3$). The crucial step of these reactions is an amido-lithiation (a nucleophilic addition of lithium anilide) of the C=N double bond in the structure of the ligands $L^{1,2}$, which is most probably activated by the strong N→B intramolecular interaction.

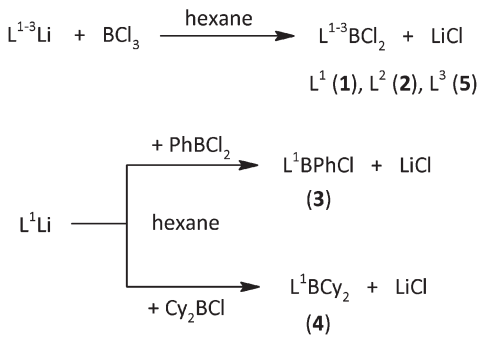
Results and discussion

Syntheses and structures of starting compounds 1–5

Compounds **1–4** (Scheme 1) have been synthesized using a well documented procedure based on the reaction between organolithium precursors and (organo)boron halides.[15] Compound **5** was prepared according to the literature procedure.[16] All compounds were obtained as stable crystalline solids in good yields (82% – **1**, 75% – **2**, 85% – **3**, 77% – **4**), which can be stored for a long time under an inert atmosphere. **1–5** are highly soluble in chlorinated solvents and showed only limited solubility in aromatic solvents, hexane and pentane.

The identity of **1–4** was unambiguously established with the help of elemental analysis and ^1H, ^{10}B,[17] ^{13}C and ^{15}N NMR spectroscopy (see the Experimental section). The molecular structures of **1**, **3–5** were determined with the help of single crystal X-ray diffraction analyses and are depicted in Fig. 3 and 4 together with selected structural parameters given in the figure captions. The crystallographic data of **1**, **3–5** are summarized in the Experimental section.

The common feature of molecular structures of **1**, **3–5** is the presence of intramolecular N→B interaction, which are characterized by the N–B bond distances 1.602(4) Å for **1**, 1.632(3) Å for **3**, 1.689(2) Å for **4**, 1.634(2) Å for **5**. The N–B bond distances become slightly longer going from **1** to **3** and **4** reflecting lowering of the Lewis acidity of the central boron atom in this set of compounds, which results in an attenuation of the N→B interaction. Nevertheless, all B–N bond distance values still approach the sum of covalent radii Σ_{cov}(N,B) = 1.56 Å[18] and correspond to the values observed for other structurally characterized *C*,*N*-chelated boranes.[15] Toyota and co-workers[19] and later on Hopfl[20] developed a concept to gauge the strength of donor–acceptor bonds in amine–borane complexes known as percent tetrahedral character (%THC). This approach was



Scheme 1 Preparation of the starting *C*,*N*-chelated boranes **1–5**.

This journal is © The Royal Society of Chemistry 2013

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

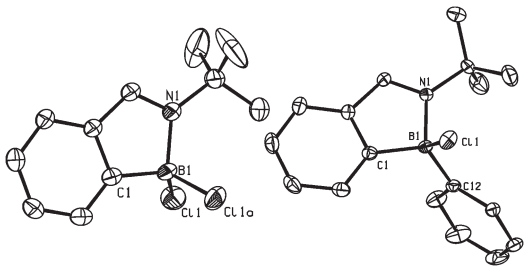


Fig. 3 ORTEP plot of a molecule of **1** (left) and **3** (right) showing 40% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity. Only one position of the disordered *t*Bu moiety is shown in the case of **1** (see experimental for details). Selected bond lengths [Å] and bonding angles [°]: For **1** (symmetry operator *a* = *x*, 1/2 − *y*, *z*): B(1)–C(1) 1.583(4), B(1)–N(1) 1.602(4), B(1)–Cl(1) 1.8582(17), N(1)–B(1)–C(1) 99.7(2), N(1)–B(1)–Cl(1) 109.92(15), C(1)–B(1)–Cl(1) 112.64(14), Cl(1)–B(1)–Cl(1a) 111.45(14). For **2**: B(1)–C(1) 1.602(3), B(1)–N(1) 1.632(3), B(1)–Cl(1) 1.893(2), B(1)–C(12) 1.598(3), N(1)–B(1)–C(1) 97.93(14), N(1)–B(1)–Cl(1) 107.09(12), N(1)–B(1)–C(12) 114.23(15), C(1)–B(1)–Cl(1) 107.74(13), C(1)–B(1)–C(12) 115.92(15), C(12)–B(1)–Cl(1) 112.66(14).

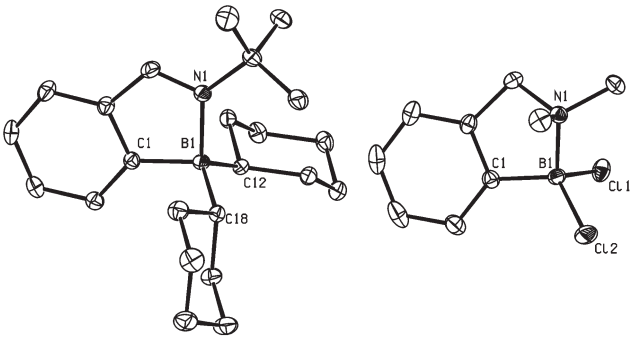
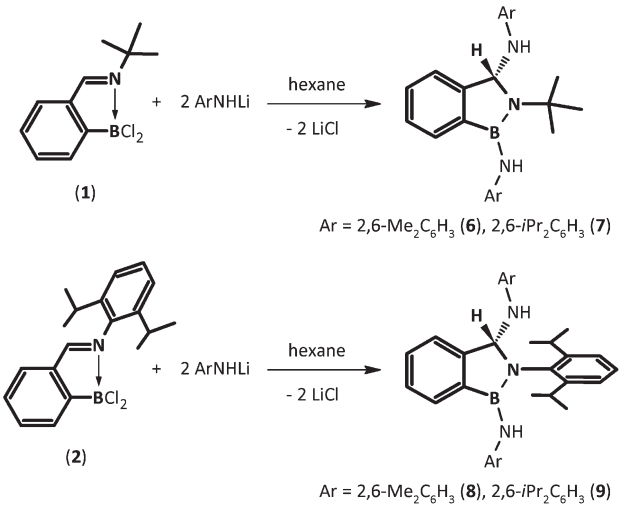


Fig. 4 ORTEP plot of a molecule of **4** (left) and **5** (right) showing 40% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bonding angles [°]: For **4**: B(1)–C(1) 1.612(3), B(1)–N(1) 1.689(2), B(1)–C(12) 1.641(2), B(1)–C(18) 1.641(2), N(1)–B(1)–C(1) 95.79(12), N(1)–B(1)–C(12) 113.58(14), N(1)–B(1)–C(18) 110.69(13), C(1)–B(1)–C(12) 108.64(13), C(1)–B(1)–C(18) 112.77(15), C(12)–B(1)–C(18) 114.01(13). For **5**: B(1)–C(1) 1.578(2), B(1)–N(1) 1.634(2), B(1)–Cl(1) 1.8664(18), B(1)–Cl(2) 1.8464(19), N(1)–B(1)–C(1) 99.56(12), N(1)–B(1)–Cl(1) 107.82(11), N(1)–B(1)–Cl(2) 111.49(11), C(1)–B(1)–Cl(1) 111.10(12), C(1)–B(1)–Cl(2) 117.30(12), Cl(1)–B(1)–Cl(2) 108.97(9).



Scheme 2 Preparation of **6–9**.

applied also to compounds **1**, **3–5**. The %THC values in the series **1** (79.0%), **3** (66.6%) and **4** (69.3%) indicate an attenuation of the present N→B interaction in this set of compounds. The %THC value for **5** of 73.8% is significantly lower than for the corresponding dichloro-complex **1** suggesting that the N→B interaction is a bit stronger in the case of **1**. This is most probably caused in part by better donating properties of imino- (**1**) than amino- (**5**) functionality and also reflects the presence of an sp^3 nitrogen atom in **5** placing both methyl groups right beside the chlorine atoms on the boron atom (rather than between the boron substituents as in the case of **1**).

Reactivity of compounds 1, 2 and 5

The reaction of dichloroboranes **1**, **2** and **5** with two equivalents of lithium anilides ArNHLi (Ar = 2,6-$Me_2C_6H_3$ or 2,6-$iPr_2C_6H_3$) was studied with the aim of formation of bis(arylamino)boranes, which would be substituted at the boron atom by chelating ligands L^{1-3}. No reaction was observed between **5** and ArNHLi even when an excess of the lithium reagent was used at elevated temperatures and only the starting material **5** was detected in the reaction mixture or after workup as a major isolable product. In contrast, the reaction between **1** or **2** and anilides ArNHLi proceeded smoothly (Scheme 2) to give substituted 1*H*-2,1-benzazaboroles **6–9** that were observed after workup instead of targeted bis(arylamino)boranes (68% – **6**, 81% – **7**, 66% – **8**, 55% – **9**). All 1*H*-2,1-benzazaboroles **6–9** were isolated as colourless solids which are stable for a long time under an inert atmosphere. All compounds were fully characterized using multinuclear NMR spectroscopy (see the Experimental section). The molecular structures of **6–9** were unambiguously established with the help of X-ray diffraction analyses. The molecular structures are given in Fig. 5 and 6. The crystallographic data of **6–9** are summarized in the Experimental section.

We are fully aware about the presence of the chiral center (at the C(7) atom) in the molecular structures of **6–9**, but all compounds crystallized in the centrosymmetric space group $P2_1/c$ as racemates.

The molecular structures of **6–9** proved the formation of benzene fused azaborole rings. The central ring systems are essentially planar in all cases. Both boron B(1) and nitrogen N(3) atoms adopt a planar environment consistent with the sp^2 hybridization within the five-membered ring as the sum of the angles around both atoms is close to the ideal value of 360°. The B(1)–N(3) bond lengths in **6–9** are apparently shorter than the sum of covalent radii for single bond Σ_{cov}(N,B) = 1.56 Å[18] and correspond to the value for the respective double bond (1.48 Å)[18] (B(1)–N(3) bond distances are 1.431(3) Å for **6**, 1.429(4) Å for **7**, 1.429(4) Å for **8**, 1.422(4) Å for **9**). This fact proves a multiple character of these bonds and reflects strong π–π interaction between both bonding partners. Similarly, the B(1)–N(2) bond distances in **6–9** (1.401(3) Å for **6**, 1.407(4) Å for **7**,

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

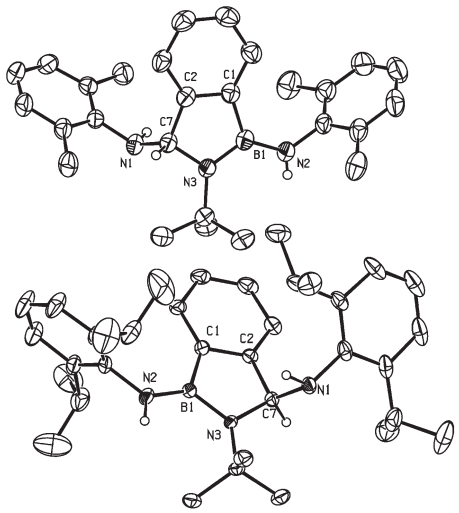


Fig. 5 ORTEP plot of a molecule of **6** (up) and **7** (bottom) showing 40% probability displacement ellipsoid. Hydrogen atoms except NH and C(7)H groups are omitted for clarity. Selected bond lengths [Å] and bonding angles [°]: For **6**: B(1)–C(1) 1.568(4), B(1)–N(3) 1.431(3), B(1)–N(2) 1.401(3), C(1)–C(2) 1.390(3), C(2)–C(7) 1.510(3), C(7)–N(3) 1.460(3), C(1)–B(1)–N(2) 126.9(2), C(1)–B(1)–N(3) 105.9(2), N(2)–B(1)–N(3) 127.2(2). For **7**: B(1)–C(1) 1.570(4), B(1)–N(3) 1.429(4), B(1)–N(2) 1.407(4), C(1)–C(2) 1.397(4), C(2)–C(7) 1.513(4), C(7)–N(3) 1.455(4), C(1)–B(1)–N(2) 127.2(2), C(1)–B(1)–N(3) 106.3(2), N(2)–B(1)–N(3) 126.6(2).

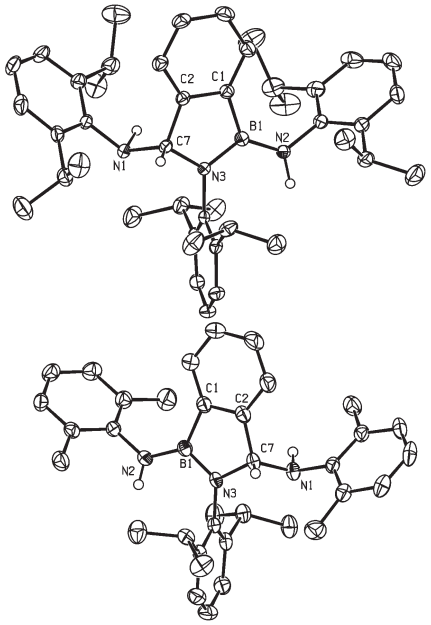


Fig. 6 ORTEP plot of a molecule of **9** (up) and **8** (bottom) showing 40% probability displacement ellipsoid. Hydrogen atoms except NH and C(7)H groups are omitted for clarity. Selected bond lengths [Å] and bonding angles [°]: For **8**: B(1)–C(1) 1.561(3), B(1)–N(3) 1.429(4), B(1)–N(2) 1.409(3), C(1)–C(2) 1.405(4), C(2)–C(7) 1.511(3), C(7)–N(3) 1.466(3), C(1)–B(1)–N(2) 130.7(2), C(1)–B(1)–N(3) 105.8(2), N(2)–B(1)–N(3) 123.5(2). For **9**: B(1)–C(1) 1.562(4), B(1)–N(3) 1.422(4), B(1)–N(2) 1.404(4), C(1)–C(2) 1.401(4), C(2)–C(7) 1.513(4), C(7)–N(3) 1.463(3), C(1)–B(1)–N(2) 130.1(3), C(1)–B(1)–N(3) 105.6(2), N(2)–B(1)–N(3) 124.3(3).

1.409(3) Å for **8**, 1.404(4) Å for **9**) point to a similar π–π interaction and N(2) atoms are coplanar with the ring system again reflecting sp^2 hybridization at boron atoms B(1). Both B(1)–N(3) and B(1)–N(2) distances are significantly shorter than the value observed for intramolecular N→B interactions in the precursor **1** (1.602(4) Å). In contrast, the remaining nitrogen atoms N(1) are bent away from the central plane in **6–9** reflecting the tetrahedral array at the C(7) carbon atom.

The solution structures of **6–9** were studied with the help of multinuclear NMR spectroscopy and all obtained data are summarized in Table 1. As all flanking NH–Ar or Ar groups (Ar = 2,6-$Me_2C_6H_3$ or 2,6-$iPr_2C_6H_3$) present in the structures of **6–9** are non-equivalent, rather complicated sets of data were observed (for full assignment see ESI†). Only one set of signals was observed in all NMR spectra of **6–9**, although they contain a chiral center (at the C(7) atom as labeled in molecular structures or at the position 3 according to IUPAC nomenclature – Table 1). All observed NMR data are entirely consistent with molecular structures as obtained for **6–9** with the help of X-ray diffraction analysis in the solid. The ^{1}H NMR spectra revealed a typical signal for the aliphatic CH group in the position 3 of the 1*H*-2,1-benzazaborole core (at 5.74 ppm for **6**; 5.70 ppm for **7**; 5.77 ppm for **8** and 5.64 ppm for **9**).[12] These values are significantly upfield shifted in comparison with the imine CH group in the starting compounds **1** and **2** (at 7.55 ppm for **1** and 8.35 for ppm **2**). Another proof for the formation of 1*H*-2,1-benzazaborole cycles is the detection of doublets (at 2.96 ppm for **6**; 3.26 ppm for **7**; 3.41 ppm for **8** and 3.46 ppm for **9**) assigned to hydrogen atoms from NH groups directly bonded to the CH groups in position 3 of 1*H*-2,1-benzazaborole cycles and also observation of singlets (at 4.04 ppm for **6**; 4.33 ppm for **7**; 3.78 ppm for **8**; 3.96 ppm for **9**) proving the presence of the second NH group bonded to the boron atom. Similarly, the ^{13}C NMR spectra established the presence of a CH group in the position 3 of the 1*H*-2,1-benzazaborole core (at 75.9 ppm for **6**; 78.7 ppm for **7**; 80.7 ppm for **8** and 83.7 ppm for **9**).[12] We decided to measure ^{10}B NMR spectra since Király observed recently[17] that the background signals arising from the NMR probe and tube are practically invisible in solution ^{10}B NMR spectra, contrary to the more sensitive ^{11}B NMR spectra. The ^{10}B NMR spectra (see the Experimental section) of **6–9** showed one signal in all cases (at 29.5 ppm for **6**; 29.5 ppm for **7**; 29.7 ppm for **8** and 30.0 ppm for **9**), which are shifted upfield ($\Delta\delta \sim 23$ ppm) in comparison to the starting compounds **1** and **2** (at 6.5 ppm for **1**; 6.8 ppm for **2**) reflecting a change of the hybridization of the boron atom from sp^3 to sp^2.[6a,d] The ^{10}B NMR chemical shifts in **6–9** are consistent with ^{11}B NMR chemical shifts of already prepared 1*H*-2,1-benzazaboroles with an N-substituent directly bonded to the boron atom.[8c] The ^{15}N NMR spectra together with $^1J(^{15}N, ^1H)$ coupling constants (Table 1) of **6–9** were measured for completeness. Three signals of different nitrogen atoms appeared in the ^{15}N NMR spectra. Two of them showed coupling with the hydrogen atom proving the presence of two NH groups.

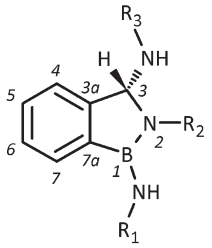
Reactivity of compounds 3 and 4

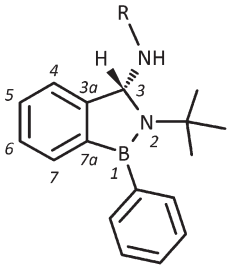
As the reaction between **1** (**2**) and lithium anilides resulted in an unexpected addition of anilides across the C=N bond

 This journal is © The Royal Society of Chemistry 2013

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

Table 1 ^{1}H, ^{10}B, ^{13}C and ^{15}N NMR data (δ = [ppm], J = [Hz]) of the central cores of **6–11** and **13** in C_6D_6 at 298 K with the numbering scheme of the 1*H*-2,1-benzazaborole cycles





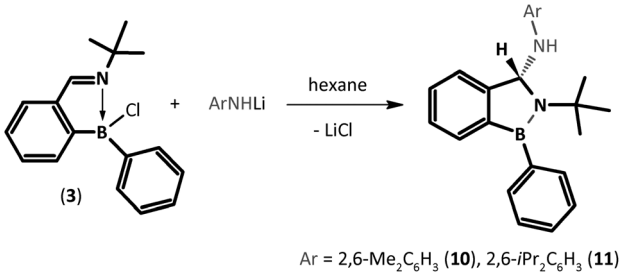
6: $R_1 = R_3 = 2,6\text{-}Me_2C_6H_3$, $R_2 = t$Bu
7: $R_1 = R_3 = 2,6\text{-}i Pr_2C_6H_3$, $R_2 = t$Bu
8: $R_1 = R_3 = 2,6\text{-}Me_2C_6H_3$, $R_2 = 2,6\text{-}i Pr_2C_6H_3$
9: $R_1 = R_2 = R_3 = 2,6\text{-}i Pr_2C_6H_3$
13: $R_1 = R_2 = 2,6\text{-}i Pr_2C_6H_3$, $R_3 = t$Bu

10: $R = 2,6\text{-}Me_2C_6H_3$
11: $R = 2,6\text{-}i Pr_2C_6H_3$

	Compound						
Position	**6**	**7**	**8**	**9**	**10**	**11**	**13**
1/δ ^{10}B	29.5	29.5	29.7	30.0	42.2	42.2	29.0
2/δ ^{15}N	−268.4	−267.2	−280.3	−280.2	−223.7	−223.3	−324.6
3/δ ^{1}H	5.74 (d)	5.70 (d)	5.77 (d)	5.64 (d)	5.92 (d)	5.90 (d)	5.38 (d)
(δ ^{13}C)	(75.9)	(78.7)	(80.7)	(83.7)	(78.4)	(81.0)	(79.0)
3a/δ ^{13}C	[a]	[a]	[a]	[a]	[a]	[a]	[a]
4/δ ^{1}H	6.22 (d)	6.12 (d)	6.87 (d)	6.57 (d)	6.36 (d)	6.23 (d)	7.38 (d)
(δ ^{13}C)	(121.9)	(122.4)	(122.9)	(123.2)	(121.8)	(122.3)	(123.5)
5/δ ^{1}H	6.68 (td)	6.60 (td)	6.89 (m)	6.77 (td)	6.85 (td)	6.78 (td)	7.16 (m)
(δ ^{13}C)	(128.3)	(127.7)	(129.8)	(129.0)	(129.2)	(128.8)	(129.8)
6/δ ^{1}H	6.76 (td)	6.70 (td)	6.91 (m)	6.81 (td)	7.04 (td)	7.01 (td)	6.94 (td)
(δ ^{13}C)	(127.6)	(127.2)	(128.5)	(127.9)	(128.1)	(128.0)	(127.7)
7/δ ^{1}H	6.56 (dt)	6.41 (dt)	6.97 (dt)	6.59 (dt)	7.40 (dt)	7.40 (dt)	6.65 (dt)
(δ ^{13}C)	(130.2)	(131.1)	(130.9)	(132.0)	(131.8)	(131.8)	(131.2)
7a/δ ^{13}C	152.6	151.8	154.8	153.2	152.7	151.9	155.9
B–NH/δ ^{1}H	4.04 (s)	4.33 (s)	3.78 (s)	3.96 (s)	—	—	3.77 (s)
(δ ^{15}N)	(−302.0)	(−307.1)	(−307.6)	(−313.6)	—	—	(−315.0)
^{1}J (^{15}N,^{1}H)	81.0	80.4	82.0	81.2	—	—	81.3
CH–NH/δ ^{1}H	2.96 (d)	3.26 (d)	3.41 (d)	3.46 (d)	3.09 (d)	3.42 (d)	1.18 (d)
(δ ^{15}N)	(−293.4)	(−292.8)	(−303.4)	(−300.8)	(−300.1)	(−297.6)	(−306.5)
^{1}J (^{15}N,^{1}H)	70.7	69.3	72.3	68.6	71.3	70.5	75.6

[a] Signal of the carbon atom 3a was not observed. s = singlet, d = doublet, td = triplet of doublets, dt = doublet of triplets, m = multiplet.

yielding 1*H*-2,1-benzazaboroles, it seemed to be reasonable to investigate similar reactions with compounds containing different substituents at the central boron atom. Thus, the reaction of **3** with one equivalent of lithium anilides ArNHLi (Ar = $2,6\text{-}Me_2C_6H_3$ or $2,6\text{-}iPr_2C_6H_3$) was studied and proceeded also as an addition of anilide giving 1*H*-2,1-benzazaboroles **10** and **11** (Scheme 3), similarly to analogous reactions of **1** and **2**. No reaction was obtained between **4** and ArNHLi even under forcing reaction conditions using elevated temperatures and an excess of ArNHLi (see further discussion). The 1*H*-2,1-benzazaboroles **10** and **11** were observed after workup in moderate yields (62% – **10**, 61% – **11**). Both compounds were fully characterized using multinuclear NMR spectroscopy (see the Experimental section). The molecular structure of **10** was unambiguously established with the help of X-ray diffraction analyses and the molecular structure is given in Fig. 7. The crystallographic data of **10** are given in the Experimental section.



Scheme 3 Preparation of **10** and **11**.

Compound **10** crystallized as a racemate in the centrosymmetric space group $P2_1/c$. The molecular structure of **10** is closely related to those found for **6–9**. The central ring system is again almost ideally planar with the significant π–π interaction between boron and nitrogen atoms within the five-membered azaborole ring as demonstrated by a rather short B

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

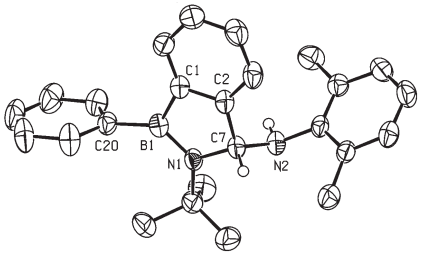


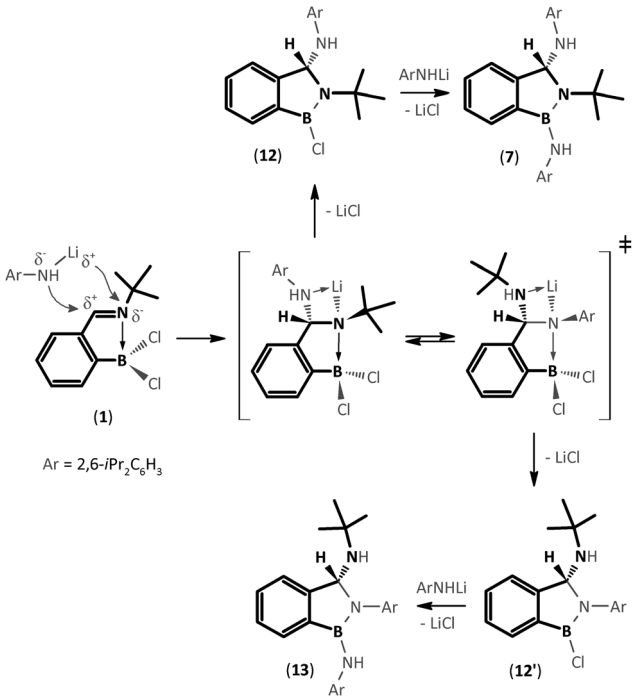
Fig. 7 ORTEP plot of a molecule of **10** showing 40% probability displacement ellipsoid. Hydrogen atoms except NH and C(7)H groups are omitted for clarity. Selected bond lengths [Å] and bonding angles [°]: B(1)–C(1) 1.557(3), B(1)–N(1) 1.406(3), C(1)–C(2) 1.392(3), C(2)–C(7) 1.516(3), C(7)–N(1) 1.480(2), C(1)–B(1)–N(1) 106.76(16), C(1)–B(1)–C(20) 123.05(20), C(1)–B(1)–C(20) 130.19(17).

(1)–N(1) bond distance of 1.406(3) Å. The second nitrogen atom N(2) is again bent out from the central plane being coordinated to the carbon atom C(7), while the *ipso*-carbon atom C(20) of the phenyl ring remains in this plane reflecting the sp^2 hybridization of the boron atom.

The structure of **10**, as determined in the solid state, is retained in solution and also the structure of **11** is analogous, as clearly established with the help of ^{1}H, ^{10}B, ^{13}C and ^{15}N NMR spectroscopy. The situation in ^{1}H and ^{13}C NMR spectra for **10** and **11** corresponds with the description made before for **6–9**. The closure of the 1*H*-2,1-benzazaborole cycle in **10** and **11** was confirmed by appearance of a doublet for aliphatic CH groups in the position 3 of the 1*H*-2,1-benzazaborole cycle in the ^{1}H NMR spectra (at 5.92 ppm for **10** and 5.90 ppm for **11**) and furthermore the doublet of NH groups directly bonded to this CH group was detected for both compounds (at 3.09 ppm for **10** and 3.42 ppm for **11**). Similarly, the presence of a CH group was corroborated by the ^{13}C NMR spectra. The ^{10}B NMR spectra also showed one signal (at 42.2 ppm for **10** and 42.2 ppm for **11**). Values of chemical shifts are about ~10 ppm downfield shifted in comparison with the values for **6–9**. The boron atoms in **10** and **11** exhibit lower electron density[6a,d] caused by a B-bonded phenyl group in comparison to **6–9** where π–π interaction between boron and nitrogen atoms leads to an increase of the electron density of the boron atoms. Nevertheless, these values are comparable to those found in analogous B-phenyl substituted 1*H*-2,1-benzazaboroles.[12] The ^{15}N NMR spectra showed only 2 signals (Table 1) for each compound, and one of them corresponds to the NH group, which is consistent with the proposed structure.

Unexpected addition reaction

Recently, we have discovered a similar cyclization procedure in a diorganoantimony compound containing ligand L^2. In this case, the first step was the formation of an antimony hydride, which then rearranged to the cyclized compound *via* hydrogen migration.[5c] In contrast, the attack of the C=N double bond (amidolithiation) in the structure of starting compounds **1–3** with subsequent elimination of lithium chloride resulting in the ring closure and formation of an intermediate **12** according to Scheme 4 is a more probable mechanism for formation



Scheme 4 Plausible mechanism for formation of studied 1*H*-2,1-benzazaboroles **7** and **13**.

of 1*H*-2,1-benzazaboroles **6–11**. A similar reaction pathway was discovered by Młynarz *et al.*, who reported an addition of diethyl phosphite across the C=N double bond in structurally related boronic acids.[13] In the case of the formation of **6–9**, the whole reaction is then terminated by the substitution of the remaining chlorine atom at the boron center with the second equivalent of the lithium anilide (see Scheme 4, where the mechanism is illustrated for the reaction between **1** and 2,6-$iPr_2C_6H_3NHLi$). Interestingly, compound L^3BCl_2 (**5**), which is void of any C=N double bond, is inert to ArNHLi under the same reaction conditions. This fact supports our presumption that the nucleophilic attack of the C=N double bond is the first step in the reaction of **1–3** with ArNHLi (Scheme 4).

Although many attempts were performed to isolate the intermediate **12** especially using the reaction between **1** and ArNHLi (Ar = 2,6-$iPr_2C_6H_3$) in a 1 : 1 molar ratio in various solvents and at different temperatures majority (see further discussion) of them failed and only the cyclized product **7** together with one half of unreacted starting material **1** were isolated and characterized with the help of multinuclear NMR spectroscopy. The first step is formation of intermediate **12** that contains cyclic systems with the B–Cl bond. This chlorine atom is most probably much more reactive than the chlorine atoms or the CH=N bond in the starting material **1** and smoothly reacts with the second molecule of the lithium anilide (of the starting one equivalent) to give final product **7** leaving half an equivalent of the starting **1** unreacted in the reaction mixture (established by NMR spectroscopy). It is noteworthy that the boron atom changes its hybridization from formally sp^3 in the starting **1** to sp^2 after cyclization to **12**.

 This journal is © The Royal Society of Chemistry 2013

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

The high reactivity of similar B–Cl bonds towards lithium reagents in analogous five-membered azaborole systems and their low stability were documented in the literature[7b] and thus it supports our suggestions of the mechanism illustrated in Scheme 4.

Interestingly, when the reaction between **1** and ArNHLi (Ar = 2,6-iPr$_2$C$_6$H$_3$) in a 1 : 1 molar ratio was performed at low temperatures (−80 °C) in toluene second product **13** besides **7** was detected in the reaction mixture and was isolated after workup as a pure compound (Scheme 4). Compound **13** again represents the product of the addition reaction between **1** and 2,6-iPr$_2$C$_6$H$_3$NHLi (although the starting compounds were mixed in 1 : 1 ratio, it means that starting **1** was detected as a by-product). In this case however, the position of the nitrogen substituents is different in comparison to the analogue **7**. The plausible explanation for formation of **13** is illustrated in Scheme 4.[21] This mechanism may involve a lithium and hydrogen atom migration after the addition of the anilide across the C═N bond leading to an intermediate **12′** after elimination of lithium chloride. **12′** then reacts with the second equivalent of ArNHLi under formation of **13**. Presumably, the lithium containing addition product is stable enough only at low temperatures and, thus, has enough time to rearrange before lithium chloride elimination and this allows formation of **12′** and subsequently **13**.[21] This presumption is supported by the fact that no evidence for formation of **13** was observed, when the reaction was performed at ambient temperature.

Compound **13** was unambiguously characterized with the help of elemental analysis and ^{1}H, ^{10}B, ^{13}C and ^{15}N NMR spectroscopy (see the Experimental section). The molecular structure of **13** was determined with the help of single crystal X-ray diffraction analyses and is depicted in Fig. 8 together with selected structural parameters given in the figure captions. It is evident that the position (exocyclic) of the *t*Bu group in **13** is different in comparison to **7**, where the *t*Bu moiety is incorporated within the azaborole ring. The basic structural features of the molecular structure of **13** are similar to the structurally related analogues **6–9** and its structure will not be discussed here in more detail.

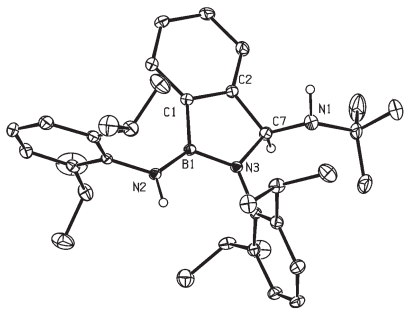


Fig. 8 ORTEP plot of a molecule of **13** showing 40% probability displacement ellipsoid. Hydrogen atoms except NH and C(7)H groups are omitted for clarity. Selected bond lengths [Å] and bonding angles [°]: B(1)–C(1) 1.564(4), B(1)–N(2) 1.409(3), B(1)–N(3) 1.420(3), C(1)–C(2) 1.402(3), C(2)–C(7) 1.521(4), C(7)–N(3) 1.481(3), C(1)–B(1)–N(3) 105.7(2), C(1)–B(1)–N(2) 129.5(2), N(2)–B(1)–N(3) 124.8(2).

The presence of an effective N→B intramolecular interaction in the structure of starting boranes **1–3** seems to be also a very important point, which should be taken into account, when considering the reactivity of **1–3**. This interaction is most probably crucial for the activation of the C═N double bond toward the amidolithiation. To test this idea, the reaction of the non-substituted ligand L^{1}H with one equivalent or an excess (2.5 equiv.) of ArNHLi was performed, but no addition of the anilide across the C═N double bond was observed even after prolonged heating of the reaction mixtures and only the starting material L^{1}H was isolated.

Similarly, compound **4**, although containing ligand L^1 and weaker but still significant N→B interaction as demonstrated by the %THC value, did not react with ArNHLi. This fact may be ascribed mainly to the lack of any chlorine atom in the structure of **4** that prevents elimination of lithium chloride and closure of the azaborole ring.

Conclusions

In conclusion, we have discovered an unexpected one pot procedure for preparation of 1,2,3-trisubstituted 1*H*-2,1-benzazaboroles. The nucleophilic addition of the lithium anilides to the C═N double bond in the structure of the ligand, which is activated by the intramolecular N→B interaction, is the crucial step of the whole reaction. Further investigations focusing on such type of addition reactions in the case of similar intramolecularly coordinated organometallic compounds using various types of nucleophiles as well as central metal atoms are currently under study in our labs.

Experimental

General procedures

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried using a Pure Solv–Innovative Technology equipment. The starting compounds: BCl_3 (1 M solution in hexane), $C_6H_5BCl_2$ (97%), Cy_2BCl (1 M solution in hexane), were obtained from the commercial suppliers and used as delivered. The ligands L^{1,2} were prepared according to published procedures[22] or by analogous procedures. Compound **5** was synthesized according to the literature.[16]

NMR spectroscopy

^{1}H, ^{10}B, ^{13}C and ^{15}N NMR spectra were recorded on Bruker 500 Avance or Bruker 400 MHz spectrometers, using a 5 mm tunable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were related to the residual signals of the solvent ($CDCl_3$: $\delta(^1H)$ = 7.27 ppm and $\delta(^{13}C)$ = 77.23 ppm, C_6D_6: $\delta(^1H)$ = 7.16 ppm and $\delta(^{13}C)$ = 128.39 ppm), ^{10}B NMR spectra were related to external standard $B(OMe)_3$ ($\delta(^{10}B)$ = 18.1 ppm), ^{15}N NMR spectra were related to external neat nitromethane ($\delta(^{15}N)$ = 0.0 ppm). For compounds **1–4**, **6–11** and

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

13[21] the full assignment of all signals in all measured NMR spectra was managed with the help of various techniques including ^{1}H, $^{13}C\{^{1}H\}$ APT, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC. We decided to measure the ^{10}B isotope instead of conventional measurement of the boron isotope ^{11}B, because of appearance of background-free signals caused by an unusual isotopic effect on the signal to background ratio.[17] Nevertheless, the chemical shift of the nuclei is not influenced and is essentially the same regardless of ^{10}B or ^{11}B NMR spectra are acquired. ^{15}N NMR chemical shifts were obtained from ^{1}H–^{15}N HMBC spectra. $^{1}J(^{15}N, ^{1}H)$ coupling constants of present NH groups were measured by 1D ^{1}H–^{15}N gs HMQC. Table 1 summarizes all NMR data of the central cores for **6–11** including the multiplicities of the signals in the ^{1}H NMR spectra. Thus, these NMR data are not again repeated in the syntheses description for respective compounds. The full assignment including assignment of all bonded aryl/alkyl groups bonded to central cores are available in the ESI.†

Syntheses

Synthesis of [*o*-(CH=N*t*Bu)C$_6$H$_4$]BCl$_2$ (1). *n*BuLi (6.3 mL of 1.6 M solution in hexane, 10.1 mmol) was added to a solution of L^{1}Br (2.43 g, 10.1 mmol) in hexane (20 mL) at 0 °C and stirred for 1 h at this temperature. Additional hexane (50 mL) was added to the resulting yellow-orange suspension of the lithium compound L^{1}Li. A 1 M solution of BCl_3 in hexane (10.1 mL, 10.1 mmol) was added under intensive stirring to the suspension of the lithium compound at 0 °C. The obtained cream mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered, the filtrate was discarded and the remaining insoluble material was washed by 2 × 10 mL of hexane. The obtained insoluble material was dried *in vacuo* and extracted by dichloromethane (3 × 25 mL). The resulting suspension was filtered and the filtrate was evaporated *in vacuo* to give **1** as a pale ginger crystalline solid (isolated yield 1.99 g, 82%), decomp. p. 178 °C.

Anal. calc. for $C_{11}H_{14}BCl_2N$ (MW 241.95): C, 54.6; H, 5.8; Found: C, 54.4; H, 5.6%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.32 (9H, s, (C*H*$_3$)$_3$C), 6.92 (2H, m, Ar-*H*), 7.16 (1H, td, Ar-*H*), 7.55 (1H, s, C*H*=N), 7.83 (1H, d, Ar-*H*). $^{13}C\{^{1}H\}$ NMR (125.76 MHz, C_6D_6): δ 30.9 ((*C*H$_3$)$_3$C), 62.0 ((CH$_3$)$_3$*C*), 126.5, 128.0, 129.7, 134.6, 135.3 (Ar-*C*), 169.3 (*C*H=N), ((Ar-*C*1-B) not observed. ^{10}B NMR (42.99 MHz, C_6D_6): δ 6.5. ^{15}N NMR (40.55 MHz, C_6D_6): δ −123.9 (CH=*N*).

Synthesis of [*o*-(CH=N-2,6-iPr$_2$C$_6$H$_3$)C$_6$H$_4$]BCl$_2$ (2). *n*BuLi (4.5 mL of 1.6 M solution in hexane, 7.2 mmol) was added to a solution of L^{2}Br (2.47 g, 7.2 mmol) in hexane (20 mL) at 0 °C and stirred for 1 h at this temperature. Additional hexane (30 mL) was added to the resulting yellow-orange suspension of the lithium compound L^{2}Li. A 1 M solution of BCl_3 in hexane (7.2 mL, 7.2 mmol) was added under intensive stirring to the suspension of the lithium compound at 0 °C. The obtained ginger mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered, the filtrate was discarded and the remaining insoluble material was washed with 2 × 10 mL of hexane. The obtained insoluble material was dried *in vacuo* and extracted by dichloromethane (3 × 25 mL). The resulting suspension was filtered and the filtrate was evaporated *in vacuo* to give **2** as a pale ginger crystalline solid (isolated yield 1.86 g, 75%), decomp. p. 132 °C.

Anal. calc. for $C_{19}H_{22}BCl_2N$ (MW 346.10): C, 65.9; H, 6.4; Found: C, 66.1; H, 6.3%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (6H, d, (C*H*$_3$)$_2$CH), 1.25 (6H, d, (C*H*$_3$)$_2$CH), 3.09 (2H, sep, 2 × (CH$_3$)$_2$C*H*), 7.17 (1H, d, Ar-*H*), 7.23 (1H, dd, Ar-*H*), 7.34 (1H, dd, Ar-*H*), 7.40 (1H, td, Ar-*H*), 7.67 (2H, m, Ar-*H*), 7.80 (1H, dd, Ar-*H*), 8.35 (1H, s, C*H*=N). $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): δ 22.9 ((*C*H$_3$)$_2$CH), 26.8 ((*C*H$_3$)$_2$CH), 29.1 (2 × (CH$_3$)$_2$*C*H), 124.4, 124.5, 127.7, 128.5, 129.6, 129.8, 133.9, 136.1, 142.8, 144.5 (Ar-*C*), 173.4 (*C*H=N), (Ar-*C*1-B) not observed. ^{10}B NMR (42.99 MHz, $CDCl_3$): δ 6.8.

Synthesis of [*o*-(CH=N*t*Bu)C$_6$H$_4$]B(C$_6$H$_5$)Cl (3). *n*BuLi (22.0 mL of 1.6 M solution in hexane, 35.2 mmol) was added to a solution of L^{1}Br (8.46 g, 35.2 mmol) in hexane (80 mL) at 0 °C and stirred for 1 h at this temperature. Additional hexane (80 mL) was added to the resulting yellow-orange suspension of the lithium compound. A solution of $C_6H_5BCl_2$ (5.60 g, 35.2 mmol) in hexane (10 mL) was added under intensive stirring to the suspension of lithium compound at 0 °C. The obtained ivory mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered, the filtrate was discarded and the remaining insoluble material was washed with 2 × 10 mL hexane. The obtained insoluble material was dried *in vacuo* and extracted by dichloromethane (3 × 25 mL). The resulting suspension was filtered and the filtrate was evaporated *in vacuo* to give **3** as an ivory crystalline solid (isolated yield 8.46 g, 85%), decomp. p. 165 °C.

Anal. calc. for $C_{17}H_{19}BClN$ (MW 283.60): C, 72.0; H, 6.8; Found: C, 72.2; H, 6.9%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.09 (9H, s, (C*H*$_3$)$_3$C), 6.94 (1H, td, Ar-*H*), 7.10 (1H, td, Ar-*H*), 7.16 (2H, m, Ar-*H*), 7.25 (2H, td, Ar-*H*), 7.50 (1H, d, Ar-*H*), 6.67 (2H, d, Ar-*H*), 7.84 (1H, s, C*H*=N). $^{13}C\{^{1}H\}$ NMR (125.76 MHz, C_6D_6): δ 31.1 ((*C*H$_3$)$_3$C), 61.3 ((CH$_3$)$_3$*C*), 126.2, 127.0, 127.2, 128.2, 130.3, 132.7, 134.4, 136.4 (Ar-*C*), 143.6 (Ph-*C*1-B), 164.7 (Ar-*C*1-B), 169.2 (*C*H=N). ^{10}B NMR (42.99 MHz, C_6D_6): δ 6.1. ^{15}N NMR (40.55 MHz, C_6D_6): δ −115.4 (CH=*N*).

Synthesis of [*o*-(CH=N*t*Bu)C$_6$H$_4$]B(C$_6$H$_{11}$)$_2$ (4). *n*BuLi (7.8 mL of 1.6 M solution in hexane, 12.5 mmol) was added to a solution of L^{1}Br (3.00 g, 12.5 mmol) in hexane (40 mL) at 0 °C and stirred for 1 h at this temperature. Additional hexane (50 mL) was added to the resulting yellow-orange suspension of the lithium compound. A 1 M solution of $(C_6H_{11})_2BCl$ in hexane (12.5 mL, 12.5 mmol) was added under intensive stirring to the suspension of the lithium compound at 0 °C. The obtained ivory mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered and the filtrate was stored at −30 °C to give the first crop of **4**. The remaining insoluble material after reaction was dried *in vacuo* and extracted by dichloromethane (3 × 30 mL). The resulting suspension was filtered and the filtrate was evaporated *in vacuo* to give the second crop of **4** as a white crystalline solid (isolated yield 3.25 g, 77%), m.p. 157 °C.

 This journal is © The Royal Society of Chemistry 2013

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

Anal. calc. for $C_{23}H_{36}BN$ (MW 337.35): C, 81.9; H, 10.8; Found: C, 82.1; H, 10.6%. ^{1}H NMR (500 MHz, C_6D_6): 0.78 (2H, qd, Cy-*H*), δ 1.17 (9H, s, $(CH_3)_3C$), 1.23–1.47 (12H, m, Cy-*H*), 1.77 (2H, dd, Cy-*H*), 1.83 (2H, dd, Cy-*H*), 1.93 (2H, dd, Cy-*H*), 2.04 (2H, d, Cy-*H*), 7.10 (1H, td, Ar-*H*), 7.31 (2H, m, Ar-*H*), 7.74 (1H, d, Ar-*H*), 7.91 (1H, s, C*H*=N). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ 28.7, 29.9, 30.4 (Cy-*C*), 31.1 ($(CH_3)_3C$), 32.0, 32.2 (Cy-*C*), 33.0 (Cy-*C*1-B), 59.7 ($(CH_3)_3C$), 125.0, 125.7, 130.5, 131.1, 138.3 (Ar-*C*), 165.7 (*C*H=N), 170.5 (Ar-*C*1-B). ^{10}B NMR (42.99 MHz, C_6D_6): δ 8.0. ^{15}N NMR (40.55 MHz, C_6D_6): δ −109.6 (CH=*N*).

Synthesis of racemic 1,3-(NH-2,6-$Me_2C_6H_3$)$_2$-2-*t*Bu-1*H*-2,1-benzazaborole (6). *n*BuLi (4.1 mL of 1.6 M solution in hexane, 6.6 mmol) was added to a solution of 2,6-dimethylaniline (803 mg, 6.6 mmol) in hexane (20 mL) at 0 °C. The obtained white suspension of lithium anilide was stirred for 30 min at 0 °C. A finely divided suspension of **1** (802 mg, 3.3 mmol) in hexane (40 mL) (**1** was partially dissolved under intensive stirring in boiling hexane, then cooled to 0 °C) was added to the suspension of the lithium anilide at 0 °C. After 15 min the reaction mixture was allowed to reach r.t. and stirred overnight. The resulting ivory suspension was filtered to give a pale yellow filtrate and the insoluble material was extracted by additional hexane (10 mL). The filtrate volume was concentrated to incipient crystallization and slow cooling to 5 °C gave colorless crystals of **6** (isolated yield 932 mg, 68%), m.p. 134 °C.

Anal. calc. for $C_{27}H_{34}BN_3$ (MW 411.39): C, 78.8; H, 8.3; Found: C, 80.0; H, 8.5%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1,3-(NH-2,6-i$Pr_2C_6H_3$)$_2$-2-*t*Bu-1*H*-2,1-benzazaborole (7). Compound **7** was prepared analogously to the procedure described for **6**. *n*BuLi (3.0 mL of 1.6 M solution in hexane, 4.8 mmol) and 2,6-diisopropylaniline (851 mg, 4.8 mmol) gave corresponding lithium anilide that was reacted with **1** (581 mg, 2.4 mmol). **7** was obtained in the form of colorless single crystals (isolated yield 1.01 g, 81%), m.p. 118 °C.

Anal. calc. for $C_{35}H_{50}BN_3$ (MW 523.60): C, 80.3; H, 9.6; Found: C, 80.5; H, 9.2%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1,3-(NH-2,6-$Me_2C_6H_3$)$_2$-2-(2,6-i$Pr_2C_6H_3$)-1*H*-2,1-benzazaborole (8). *n*BuLi (1.8 mL of 1.6 M solution in hexane, 2.9 mmol) was added to a solution of 2,6-dimethylaniline (357 mg, 2.9 mmol) in hexane (20 mL) at 0 °C. The obtained white suspension of lithium anilide was stirred for 30 min at 0 °C. A finely divided suspension of **2** (510 mg, 1.5 mmol) in hexane (40 mL) (**2** was partially dissolved under intensive stirring in boiling hexane, then cooled to 0 °C) was added to the suspension of lithium anilide at 0 °C. After 15 min the reaction mixture was allowed to reach r.t. and stirred overnight. The resulting ivory suspension was decanted and the solution was discarded. The white insoluble residue was washed with hexane (5 mL) and then extracted with benzene (30 mL). The obtained suspension was filtered to give a pale yellow filtrate. The filtrate was evaporated *in vacuo* to dryness. The obtained crude product was recrystallized from the minimal amount of hot hexane to give **8** as colorless single crystals (isolated yield 499 mg, 66%), m.p. 213 °C.

Anal. calc. for $C_{35}H_{42}BN_3$ (MW 515.54): C, 81.5; H, 8.2; Found: C, 81.3; H, 8.0%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1,3-(NH-2,6-i$Pr_2C_6H_3$)$_2$-2-(2,6-i$Pr_2C_6H_3$)-1*H*-2,1-benzazaborole (9). Compound **9** was prepared analogously to the procedure described for **8**. *n*BuLi (2.2 mL of 1.6 M solution in hexane, 3.6 mmol) and 2,6-diisopropylaniline (636 mg, 3.6 mmol) gave corresponding lithium anilide that was reacted with **2** (620 mg, 1.8 mmol). **9** are colorless single crystals (isolated yield 623 mg, 55%), m.p. 221 °C.

Anal. calc. for $C_{43}H_{58}BN_3$ (MW 627.75): C, 82.3; H, 9.3; Found: C, 82.4; H, 9.5%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1-C_6H_5-2-*t*Bu-3-(NH-2,6-$Me_2C_6H_3$)-1*H*-2,1-benzazaborole (10). *n*BuLi (1.8 mL of 1.6 M solution in hexane, 2.9 mmol) was added to a solution of 2,6-dimethylaniline (356 mg, 2.9 mmol) in hexane (20 mL) at 0 °C. The obtained white suspension of lithium anilide was stirred for 30 min at 0 °C and after that it was added to a suspension of **3** (833 mg, 2.9 mmol) in hexane (40 mL) at 0 °C. The resulting mixture was stirred for 15 min at 0 °C and then was allowed to reach r.t. and stirred overnight. The resulting pale yellow suspension was filtered to give a pale yellow filtrate and the insoluble material was extracted by additional hexane (10 mL). The filtrate volume was concentrated to incipient crystallization and slow cooling to 5 °C gave colorless crystals of **10** (isolated yield 667 mg, 62%), m.p. 106 °C.

Anal. calc. for $C_{25}H_{29}BN_2$ (MW 368.32): C, 81.5; H, 7.9; Found: C, 81.2; H, 7.7%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1-C_6H_5-2-*t*Bu-3-(NH-2,6-i$Pr_2C_6H_3$)-1*H*-2,1-benzazaborole (11). Compound **11** was prepared analogously to the procedure described for **10**. *n*BuLi (1.2 mL of 1.6 M solution in hexane, 1.9 mmol) and 2,6-diisopropylaniline (343 mg, 1.9 mmol) gave corresponding lithium anilide that was reacted with **3** (549 mg, 1.9 mmol). Isolated yield 501 mg, 61%. Neither X-ray diffraction analysis nor melting point could be obtained, because any attempt to crystallize **11** failed. It was observed just as honey-like material that decomposes slowly over time.

Anal. calc. for $C_{29}H_{37}BN_2$ (MW 424.43): C, 82.1; H, 8.8; Found: C, 79.9; H, 8.9%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

Synthesis of racemic 1-(NH-2,6-i$Pr_2C_6H_3$)-2-(2,6-i$Pr_2C_6H_3$)-3-(NH-*t*Bu)-1*H*-2,1-benzazaborole (13). *n*BuLi (2.9 mL of 1.6 M solution in hexane, 4.7 mmol) was added to a solution of 2,6-diisopropylaniline (835 mg, 4.7 mmol) in hexane (30 mL) at 0 °C. The obtained white suspension of lithium anilide was stirred for 30 min at 0 °C and after that was added to a precooled suspension of **1** (1.14 g, 4.7 mmol) in toluene (40 mL) at −80 °C. The resulting mixture was stirred for 30 min at −80 °C and then was allowed to reach r.t. and stirred overnight. The resulting ginger suspension was filtered to give a ginger filtrate, which was evaporated *in vacuo* to give pale

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

ginger-green honey-like matter. This matter was treated with hexane (10 mL) leading to formation of a white precipitate that was isolated. The obtained white solid (containing both **1** and **13**) was extracted with the mixture of hexane (30 mL) and toluene (10 mL). The obtained pale green suspension was filtered, the residue was discarded and the filtrate was evaporated *in vacuo* to give a pale yellow powder. The obtained powder was recrystallized from boiling hexane (35 mL) to give **13** as colorless crystals (isolated yield 602 mg, 49% according to 2,6-diisopropylaniline), m.p. 187 °C. **13** is stable for a long time (several months) in an argon atmosphere.

Anal. calc. for $C_{35}H_{50}BN_3$ (MW 523.60): C, 80.3; H, 9.6; Found: C, 80.4; H, 9.5%. For NMR data of the core see Table 1 and for complete assignment see the ESI.†

X-ray crystallography

The suitable single crystals were mounted on a glass fibre with an oil and measured on a four-circle diffractometer KappaCCD with a CCD area detector by monochromatized MoK_α radiation (λ = 0.71073 Å) at 150(1) K. The numerical[23] absorption corrections from the crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92)[24] and refined by a full matrix least squares procedure based on F^2 (SHELXL97).[25] Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors H_{iso} (H) = 1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in the aromatic ring, respectively. The *t*Bu groups in **1** are disordered along the special position where a C9 methyl atom remains on the same place. This disorder has been treated by splitting of C8 *ipso* carbon – the parent carbon atom of the *t*Bu group and a C10 methyl group into two equivalent positions while C10a is symmetry related. All the crystal structures of studied compounds revealed a bit higher wR_2 parameters, which is caused by very limiting diffraction limits of even very large crystals. Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 801796–801806.

Crystallographic data for 1. $C_{11}H_{14}BCl_2N$, M = 241.94, orthorhombic, *Pnma*, a = 13.5840(3), b = 6.9169(7), c = 12.8092(7) Å, V = 1203.54(14) Å^3, Z = 4, T = 150(2) K, 7481 total reflections, 1316 independent (R_{int} = 0.023, R_1 (obs. data) = 0.044, wR_2 (all data) 0.104), S = 1.285, $\Delta\rho$, max., min. [e Å^{-3}] 0.247, −0.392, CCDC 908869.

Crystallographic data for 3. $C_{17}H_{19}BClN$, M = 283.59, orthorhombic, $P2_12_12_1$, a = 8.8400(7), b = 11.2160(7), c = 15.6841(12) Å, V = 1555.1(2) Å^3, Z = 4, T = 150(1) K, 13 296 total reflections, 3504 independent (R_{int} = 0.037, R_1 (obs. data) = 0.039, wR_2 (all data) 0.095), S = 1.110, $\Delta\rho$, max., min. [e Å^{-3}] 0.411, −0.256, CCDC 908872.

Crystallographic data for 4. $C_{23}H_{36}BN$, M = 337.34, orthorhombic, *Pbca*, a = 8.3280(6), b = 15.7381(16), c = 30.885(2) Å, V = 4048.0(6) Å^3, Z = 8, T = 150(1) K, 25 505 total reflections, 4398 independent (R_{int} = 0.041, R_1 (obs. data) = 0.059, wR_2 (all data) 0.114), S = 1.166, $\Delta\rho$, max., min. [e Å^{-3}] 0.254, −0.214, CCDC 908873.

Crystallographic data for 5. $C_9H_{12}BCl_2N$, M = 215.91, orthorhombic, $P2_12_12_1$, a = 9.4390(4), b = 9.5611(5), c = 11.6760(3) Å, V = 1053.73(8) Å^3, Z = 4, T = 150(1) K, 9643 total reflections, 2404 independent (R_{int} = 0.023, R_1 (obs. data) = 0.027, wR_2 (all data) 0.062), S = 1.122, $\Delta\rho$, max., min. [e Å^{-3}] 0.181, −0.216, CCDC 908867.

Crystallographic data for 6. $C_{27}H_{34}BN_3$, M = 411.38, monoclinic, $P2_1/c$, a = 9.8030(5), b = 17.1271(11), c = 15.1920(12) Å, β = 108.461(6), V = 2419.4(3) Å^3, Z = 4, T = 150(1) K, 17 290 total reflections, 5423 independent (R_{int} = 0.047, R_1 (obs. data) = 0.067, wR_2 (all data) 0.130), S = 1.185, $\Delta\rho$, max., min. [e Å^{-3}] 0.163, −0.209, CCDC 908866.

Crystallographic data for 7. $C_{35}H_{50}BN_3$, M = 523.59, monoclinic, $P2_1/c$, a = 13.4110(10), b = 10.3260(9), c = 26.2331(18) Å, β = 115.566(6), V = 3277.1(5) Å^3, Z = 4, T = 150(1) K, 19 620 total reflections, 6170 independent (R_{int} = 0.070, R_1 (obs. data) = 0.078, wR_2 (all data) 0.159), S = 1.109, $\Delta\rho$, max., min. [e Å^{-3}] 0.254, −0.332, CCDC 908868.

Crystallographic data for 8. $C_{35}H_{42}BN_3$, M = 515.53, monoclinic, $P2_1/c$, a = 12.5801(13), b = 15.2930(14), c = 19.0710(19) Å, β = 125.552(7), V = 2985.1(6) Å^3, Z = 4, T = 150(1) K, 23 236 total reflections, 6729 independent (R_{int} = 0.054, R_1 (obs. data) = 0.064, wR_2 (all data) 0.118), S = 1.161, $\Delta\rho$, max., min. [e Å^{-3}] 0.303, −0.242, CCDC 908865.

Crystallographic data for 9. $C_{43}H_{58}BN_3$, M = 627.73, monoclinic, $P2_1/c$, a = 10.2110(13), b = 21.1459(17), c = 18.6160(13) Å, β = 106.805(8), V = 3847.9(7) Å^3, Z = 4, T = 150(1) K, 30 030 total reflections, 8550 independent (R_{int} = 0.067, R_1 (obs. data) = 0.077, wR_2 (all data) 0.139), S = 1.175, $\Delta\rho$, max., min. [e Å^{-3}] 0.507, −0.557, CCDC 908864.

Crystallographic data for 10. $C_{25}H_{29}BN_2$, M = 368.31, monoclinic, $P2_1/c$, a = 10.3891(9), b = 10.2250(4), c = 20.5820(15) Å, β = 102.468(7), V = 2134.8(3) Å^3, Z = 4, T = 150(1) K, 19 153 total reflections, 4751 independent (R_{int} = 0.039, R_1 (obs. data) = 0.058, wR_2 (all data) 0.115), S = 1.168, $\Delta\rho$, max., min. [e Å^{-3}] 0.172, −0.206, CCDC 908870.

Crystallographic data for 13. $C_{35}H_{50}BN_3$, M = 523.59, monoclinic, $P2_1/c$, a = 8.9470(6), b = 20.765(2), c = 17.1239(15) Å, β = 98.560(7), V = 3145.9(5) Å^3, Z = 4, T = 150(1) K, 28 078 total reflections, 6984 independent (R_{int} = 0.045, R_1 (obs. data) = 0.076, wR_2 (all data) 0.159), S = 1.097, $\Delta\rho$, max., min. [e Å^{-3}] 1.112, −0.335, CCDC 908871.

Acknowledgements

The authors thank the Grant agency of the Czech Republic project no. P207/11/0223.

Notes and references

1 C. Fedorchuk, M. Copsey and T. Chivers, *Coord. Chem. Rev.*, 2007, **251**, 897.

2 For recent reviews see: (*a*) F. Edelmann, *Adv. Organomet. Chem.*, 2008, **57**, 183; (*b*) M. Asay, C. Jones and M. Driess,

 This journal is © The Royal Society of Chemistry 2013

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

Chem. Rev., 2011, **221**, 354; (*c*) S. Collins, *Coord. Chem. Rev.*, 2011, **255**, 118; (*d*) A. A. Mohamed, *Coord. Chem. Rev.*, 2010, **254**, 1918.

3 For several examples see: (*a*) T. Chivers, C. Fedorchuk and M. Parvez, *Inorg. Chem.*, 2004, **43**, 2643; (*b*) T. Chivers, C. Fedorchuk, G. Schatte and M. Parvez, *Inorg. Chem.*, 2003, **42**, 2084; (*c*) D. Fest, C. D. Habben, A. Meller, G. M. Sheldrick, D. Stalke and F. Pauer, *Chem. Ber.*, 1990, **123**, 703; (*d*) T. Albrecht, G. Elter, M. Noltemeyer and A. Meller, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1514; (*e*) A. Heine, D. Fest, D. Stalke, C. D. Habben, A. Meller and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1990, 742; (*f*) T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen and R. T. Boer'e, *Inorg. Chem.*, 2006, **45**, 2119; (*g*) T. Chivers, X. Gao and M. Parvez, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2549; (*h*) H.-J. Koch, H.W. Roesky, S. Besser and R. Herbst-Irmer, *Chem. Ber.*, 1993, **126**, 571; (*i*) D. R. Manke and D. G. Nocera, *Inorg. Chem.*, 2003, **42**, 4431; (*j*) D. R. Manke and D. G. Nocera, *Inorg. Chim. Acta*, 2003, **345**, 235; (*k*) D. R. Manke, Z.-H. Loh and D. G. Nocera, *Inorg. Chem.*, 2004, **43**, 3618.

4 (*a*) T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen and R. T. Boeré, *Inorg. Chem.*, 2006, **45**, 2119; (*b*) J. Konu, H. M. Tuononen, T. Chivers, A. M. Corrente, R. T. Boeré and T. L. Roemmele, *Inorg. Chem.*, 2008, **47**, 3823; (*c*) T. Chivers, C. Fedorchuk, G. Schatte and J. K. Brask, *Can. J. Chem.*, 2002, **80**, 821; (*d*) T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen and R. T. Boeré, *Chem. Commun.*, 2005, 3930.

5 For recent examples see: (*a*) P. Šimon, F. de Proft, R. Jambor, A. Růžička and L. Dostál, *Angew. Chem., Int. Ed.*, 2010, **49**, 5468; (*b*) L. Dostál, R. Jambor, A. Růžička and J. Holeček, *Organometallics*, 2008, **27**, 2169; (*c*) L. Dostál, R. Jambor, A. Růžička and P. Šimon, *Eur. J. Inorg. Chem.*, 2011, 2380; (*d*) M. Bouška, L. Dostál, Z. Padělková, S. Herres-Pawlis, K. Jurkschat, A. Lyčka and R. Jambor, *Angew. Chem., Int. Ed.*, 2012, **51**, 3478; (*e*) P. Šimon, R. Jambor, A. Růžička, A. Lyčka, F. De Proft and L. Dostál, *Dalton Trans.*, 2012, **41**, 5140; (*f*) M. Bouška, L. Dostál, F. De Proft, A. Růžička, A. Lyčka and R. Jambor, *Chem.–Eur. J.*, 2011, **17**, 455.

6 (*a*) G. Schmidt, *Comprehensive Heterocyclic Chemistry II*, 1996, Chapter 3.17, vol. 3, p. 739; (*b*) G. Schmidt, *Comments Inorg. Chem.*, 1985, **4**, 17; (*c*) A. J. Ashe III and X. Fang, *Org. Lett.*, 2000, **2**, 2089; (*d*) S.-Y. Liu, M.-C. Lo and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 174; (*e*) A. J. Ashe III, *Comprehensive Heterocyclic Chemistry III*, 2008, Chapter 4.17, vol. 4, p. 1189.

7 (*a*) A. J. Ashe III, *Organometallics*, 2009, **28**, 4236; (*b*) X. Fang and J. Assoud, *Organometallics*, 2008, **27**, 2408; (*c*) G. Schmidt, O. Boltsch and R. Boese, *Organometallics*, 1987, **6**, 435; (*d*) G. Schmidt and M. Schütz, *Organometallics*, 1992, **11**, 1789; (*e*) X. Fang, X. Li, Z. Hou, J. Assoud and R. Zhao, *Organometallics*, 2009, **28**, 517; (*f*) G. Schmidt and M. Schütz, *J. Organomet. Chem.*, 1995, **492**, 185; (*g*) S. Liu, M.-C. Lo and G. C. Fu, *Tetrahedron*, 2006, **62**, 11343; (*h*) X. Fang, Y. Deng, Q. Xie and F. Moingeon, *Organometallics*, 2008, **27**, 2892.

8 (*a*) S. Nagy, R. Krishnamatti and B. P. Etherton, *U.S. Patent* 6,228,959, 2001; S. Nagy, R. Krishnamatti and B. P. Etherton, *Chem. Abstr.*, 1997, **126**, 19432j; (*b*) Q. Wang, P. Zoricak and X. Gao, *Can. Patent Appl.* 2,225,014, 1999; Q. Wang, P. Zoricak and X. Gao, *Chem. Abstr.*, 1999, **142**, 219701; (*c*) M. Yamashita, Y. Aramaki and K. Nozaki, *New J. Chem.*, 2010, **34**, 1774.

9 (*a*) V. Lee, *et al.*, *U.S. Patent* 7,465,836, 2008; (*b*) V. Lee, *et al.*, *U.S. Patent* 8,106,031, 2012.

10 (*a*) R. Köster, K. Iwasaki, S. Hattori and Y. Morita, *Liebigs Ann. Chem.*, 1968, **720**, 23; (*b*) R. Köster and K. Iwasaki, *Advances in Chemistry*, 1964, Chapter 16, vol. 42, p. 148.

11 (*a*) P. T. Hawkins and A. U. Blackham, *J. Org. Chem.*, 1967, **32**, 597; (*b*) H. E. Dunn, J. C. Catlin and H. R. Snyder, *J. Org. Chem.*, 1968, **33**, 4483; (*c*) M. Lauer and G. Wulff, *J. Organomet. Chem.*, 1983, **256**, 1.

12 A. M. Genaev, S. M. Nagy, G. E. Salnikov and V. G. Shubin, *Chem. Commun.*, 2000, 1587.

13 A. Rydzewska, K. Slepokura, T. Lis, P. Kafarski and P. Młynarz, *Tetrahedron Lett.*, 2009, **50**, 132.

14 T. S. De Vries, A. Prokofjevs, J. N. Harvey and E. Vedejs, *J. Am. Chem. Soc.*, 2009, **131**, 14679.

15 For example see: (*a*) L. Horner, U. Kaps and G. Simons, *J. Organomet. Chem.*, 1985, **287**, 1; (*b*) R. Schlengermann, J. Sieler and E. Hey-Hawkins, *Main Group Met. Chem.*, 1997, **2**, 141; (*c*) Z. García-Hernández and F. P. Gabbaï, *Z. Naturforsch., B: Chem. Sci.*, 2009, **64**, 1381; (*d*) Z. M. Heiden, M. Schedler and D. W. Stephan, *Inorg. Chem.*, 2011, **50**, 1470; (*e*) M. Yamashita, K. Kamura, Y. Yamamoto and K. Akiba, *Chem.–Eur. J.*, 2002, **8**, 2976; (*f*) M. Yamashita, Y. Yamamoto, K. Akiba, D. Hashizume, F. Iwasaki, N. Takagi and S. Nagase, *J. Am. Chem. Soc.*, 2005, **127**, 4354.

16 A. Meller, H. Hoppe, W. Maringgele, A. Haase and M. Noltemeyer, *Organometallics*, 1998, **17**, 123.

17 P. Király, *Magn. Reson. Chem.*, 2012, **50**, 620.

18 (*a*) P. Pyykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 186; (*b*) P. Pyykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 12770; (*c*) P. Pyykkö, S. Riedel and M. Patzschke, *Chem.–Eur. J.*, 2005, **11**, 3511.

19 (*a*) S. Toyota and M. Oki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1832; (*b*) S. Toyota and M. Oki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2215.

20 H. Hopfl, *J. Organomet. Chem.*, 1999, **581**, 129.

21 We are grateful to one of the reviewers of this manuscript, who suggested that the lithium atom in the structure of the addition product can be coordinated either to anilido-nitrogen or imino-nitrogen or may even bridge these two atoms. Such migration of the lithium atom precisely explains formation of both compounds **7** and **13** in one reaction depending on the conditions, where especially the formation of **13** was obscure to us.

22 D. Zhao, W. Gao, Y. Mu and L. Ye, *Chem.–Eur. J.*, 2010, **16**, 4394.
23 P. Coppens, in *Crystallographic Computing*, ed. F. R. Ahmed, S. R. Hall, and C. P. Huber, Copenhagen, Munksgaard, 1970, pp. 255–270.
24 A. Altomare, G. Cascarone, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 1045.
25 G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Published on 10 January 2013. Downloaded by University of Victoria on 25/10/2014 22:45:42.

This journal is © The Royal Society of Chemistry 2013