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Modification and Unexpected Reactivity of 2-Borylbenzaldimines: Acylated and Silylated Derivatives as Well as Dimeric Compounds

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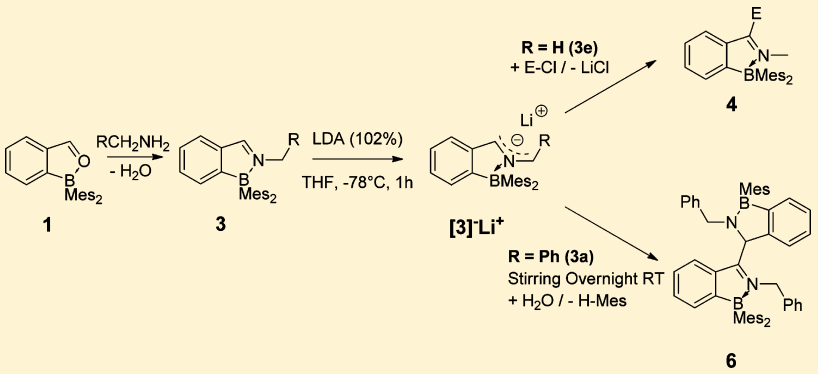
Supporting Information



ABSTRACT: Various novel *N*-alkyl and *N*-benzyl 2-borylbenzaldimines **3** were prepared by condensation of 2-(dimesitylboryl)benzaldehyde (**1**) with amines. Further functionalization of compound **3e** was possible by deprotonation and subsequent regioselective reaction with electrophiles to give compounds **4**. Applying similar conditions to **3a** led to the unexpected formation of hitherto unknown dimeric compounds (**5** and **6**). All structural types were fully characterized, including by X-ray diffraction (XRD). Furthermore, quantum chemical calculations on the SCS-MP2 and DFT levels gave insights into the reaction mechanisms and the stereoselectivity. The B/N bonding situation in these molecules was analyzed using Wiberg bond indices. Preliminary UV−vis and fluorescence measurements indicate that the substitution reaction leading to compounds **4** can be utilized to tune the photophysical properties of these compounds.

INTRODUCTION

The incorporation of main-group elements into organic materials has attracted tremendous interest in the past decade.[1−4] Boron and nitrogen are two key players used frequently in novel main-group-element-containing aromatic systems, and many research groups have shown the drastic influence of the combination of these complementary Lewis acidic and basic elements on the photophysical and electronic properties in comparison to all-carbon-containing materials.[5−18] In previous work we have focused our attention on the synthesis, molecular structures, and photophysical properties of 2-borylbenzaldimines.[19] Now, we investigate possible methods for the chemical modification of such compounds by introducing further substituents via deprotonation and electrophilic attack and so influencing the photophysical properties of the B/N systems. This is in contrast to most of the previously published syntheses, where the labile boron functionality was introduced in the last step.

Our group is well experienced in the preparation and application of anionic intermediates: e.g., by deprotonation of aza- and diazapolyenes for subsequent electrocyclic reactions[20−23] and for effective functionalization.[24] Thus, we report herein the synthesis of novel *N*-alkyl and benzyl B/N heterocyclic compounds **3** with a CH_2R group in the position α to nitrogen, allowing for deprotonation to give borylated 2-azaallyl- and 2-azapentadienyllithium compounds.[25] In the case of **3e** the lithiated intermediate was reacted regioselectively with various electrophiles, yielding the modified B/N compounds **4**, which show tunable UV−vis and fluorescence properties and photochemical reactivity. In case of **3a** a base-promoted, unusual dimerization reaction leading to the hitherto unknown bis-B/N heterocyclic compound **6** with a tri- as well as a tetravalent boron atom was observed. The experimental results are accompanied by quantum chemical calculations to give insight into the reaction mechanism and to analyze the B/N bonding (Wiberg bond indices[26]) as well as the electronic structures (NBO[27]) of these novel molecules.

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RESULTS AND DISCUSSION

Preparation and Characterization of 2-Borylbenzaldimines 3a−g. 2-(Dimesitylboryl)benzaldehyde (**1**) was used as a precursor for the synthesis of the *N*-benzyl- and *N*-alkyl-substituted 2-borylbenzaldimines **3a−g**. The synthesis of **1** was described previously by Kawashima et al. and Gabbaï et al.[16,19,28] The condensation reaction of **1**, which might be regarded as an internally Lewis acid activated aldehyde, with alkyl- and allylamines and various electron-poor and electron-rich benzylamines (**2**; 1.02−2.00 equiv) gave colorless or yellow borylbenzaldimines **3a−g** in moderate to good yields (Scheme 1, Table 1). Compounds **3a−g** show fluorescence in the solid state and in solution (see Influence of the Substitution Pattern on the Photophysical Properties).

Scheme 1. Synthesis of Compounds 3a−g

1 3a-g

Table 1. Yields of 3a−g

compd	R	yield, %
3a	Ph	90
3b	4-Cl-Ph	37
3c	4-OMe-Ph	52
3d	2,4-OMe-Ph	62
3e	H	70
3f	^{t}Bu	56
3g	CH=CH$_2$	58

We were able to grow single crystals of **3a,d−g** and to analyze their molecular structures by X-ray diffraction. Figure 1

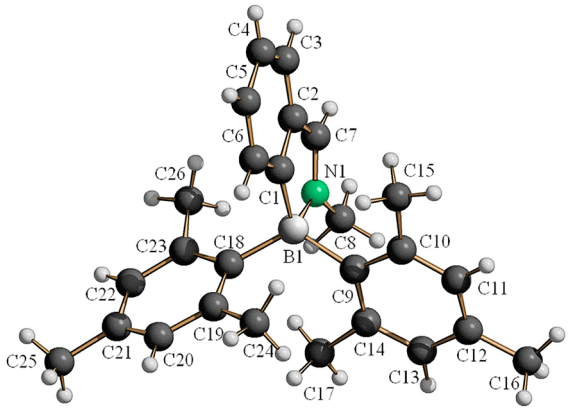


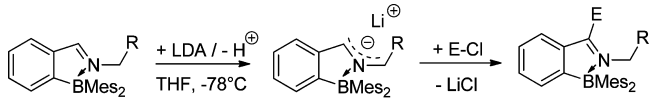
Figure 1. Molecular structure of compound **3e** in the solid state (Schakal plot).

depicts—as a typical example—the crystal structure of **3e** (for the structures of **3a,d,f,g** see the Supporting Information). The N1−B1 distance amounts to 1.645 Å, clearly indicating a coordinative interaction. A value of 1.289 Å was found for the length of the C7=N1 double bond. The Wiberg bond indices (natural bond orbital (NBO) analysis at the B3LYP/6-31G(d) level of theory) for **3e**—as an example—are 0.6459 and 1.5837 for the B1−N1 and C7=N1 bonds, respectively, quantifying this strong Lewis acid−base interaction (for NBO data of all important compounds reported in this paper see the Supporting Information).

In the ^{1}H NMR spectrum of the typical example **3b** the benzylic C*H*$_2$ protons give rise to two sets of doublets at 4.50 and 4.74 ppm (geminal coupling constant 16.0 Hz). Their diastereotopicity is due to the bulky mesityl groups causing restricted rotation about the CH$_2$−N bond. The aromatic signals are found between 6.20 and 7.86 ppm. Among these signals, two broad singlets are attributed to the aromatic protons of the mesityl groups. The iminic proton shows a resonance as a singlet at 7.55 ppm. This signal is found at high field in comparison to that of imines not coordinated to a Lewis acid. A sharp singlet at 6.79 ppm in the ^{11}B NMR spectrum (see the Supporting Information) is an indication of the presence of a tetravalent boron atom. In the ^{13}C NMR spectrum of **3b** the carbon atoms of the mesityl CH$_3$ groups show resonances between 21.0 and 27.0 ppm. The CH$_2$ group gives a signal at 54.3 ppm. Between 125.2 and 144.0 ppm the signals of the aromatic carbon atoms are detected. At 167.8 ppm the iminic carbon atom shows a resonance, which is shifted downfield from that of imines without a coordinating boron moiety. We also studied the behavior of the compound in solvents with different polarities (C_6D_6, CD_2Cl_2, and DMSO-d_6). According to the recorded spectra the coordination of nitrogen to the boron center seems not to be affected by solvent polarity. These observations indicate that the N−B heterocyclic structure is stable in polar and coordinating solvents, even in water containing DMSO. This increased stability might be advantageous, for example, for the preparation of electron-transporting materials. The NMR spectra of the other compounds **3a,c−g** are similar to those of **3b**; all of the ^{11}B NMR signals are found in the range 5−7 ppm.

Deprotonation of 2-Borylbenzaldimines 3e−g and Subsequent Reaction with Electrophiles. We were interested in further functionalizing the photoactive compounds **3** in order to modify their electronic structure and properties. Therefore, in a first series of experiments the B/N heterocycle **3e** was treated with different strong bases and subsequently reacted with electrophiles. Use of lithium diisoproylamide (LDA; 1.02 equiv) as base in tetrahydrofuran (THF), temperatures of −78 °C, and slow warming after addition of an excess of the electrophile (2.00 equiv) turned out to be the best conditions for the reaction. After the addition of the base the light yellow reaction mixture turned orange-red, indicating the formation of an intermediate anionic species; after the addition of the electrophile, the color changed back to light yellow. After aqueous workup and purification by recycling gel permeation chromatography (GPC) or recrystallization the acylated and silylated products **4a−d** were obtained (Scheme 2, Table 2)).

Scheme 2. Synthesis of Compounds 4



3e-g 4a-d

Similar to the case for **3a−g** the compounds **4a−d** also show fluorescence (see Influence of the Substitution Pattern on the Photophysical Properties). Interestingly, only one regioisomer was formed by electrophilic substitution at the aza-bora ring system (vide infra, Mechanistic Investigation/Quantum Chemical Calculations). For the typical example **4a** characteristic

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Table 2. Yields for the Synthesis of Substituted 2-Borylbenzaldimes 4

starting material	R	electrophile (E^+)	product[a]	yield, %
3e	H	*t*BuCOCl	**4a**	72
3e	H	PhCOCl	**4b**	65
3e	H	Me_3SiCl	**4c**	56
3e	H	Ph_3SiCl	**4d**	58
3f	^{t}Bu	*t*BuCOCl	*b*	
3g	$CH{=}CH_2$	*t*BuCOCl	*b*	

[a]Reaction conditions: LDA; THF, −78 °C, 1 h. [b]By NMR control the reaction was found to proceed, but isolation/purification was not possible due to the formation of multiple side products (see text).

resonances of the iminic carbon and the carbonyl carbon were found in the ^{13}C NMR spectra at 175.3 and 210.5 ppm, respectively. The boron NMR spectrum displays a sharp singlet at 5.07 ppm, which is not significantly shifted in comparison to the nonfunctionalized compound (**3e**; 5.00 ppm). Additional structural proof for the *α*-keto imine **4a** was gained by XRD (Figure 2). The C═N bond length amounts to 1.291 Å, whereas

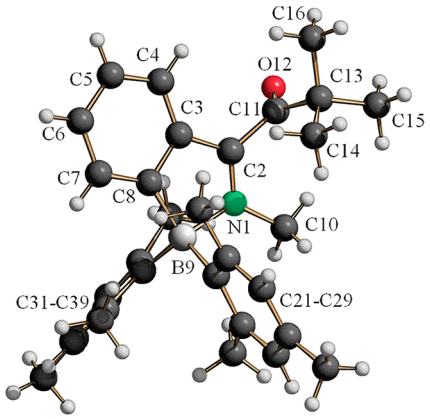


Figure 2. Molecular structure of compound **4a** in the solid state (Schakal plot).

a length of 1.654 Å is measured for the N−B bond. Obviously the functionalization at the B/N heterocyclic ring system has minor effects on the structural properties. This is also reflected in the Wiberg bond indices, which amount to 0.608 (N−B) and 1.592 (C═N).

Deprotonation of compounds **3f** (R = ^{t}Bu) and **3g** (R = CH═CH_2) and subsequent treatment with electrophiles were also investigated (Table 2). We observed a typical color change from colorless to deep blue during the deprotonation, indicating again the in situ formation of an anionic species. Addition of an electrophile changed the color to light yellow. After workup functionalized products were detected by NMR and MS control, but due to competing side reactions only complex mixtures were obtained.

Base-Promoted Dimerization of Compound 3a. In a further series of experiments we investigated the reactivity of the benzyl-substituted compound **3a** toward strong bases (Scheme 3). Upon deprotonation using LDA the solution turned deep red, and after aqueous workup and subsequent GPC the colorless solid **6** was obtained in 74% yield. Other reaction conditions turned out to be less successful (Table 3).

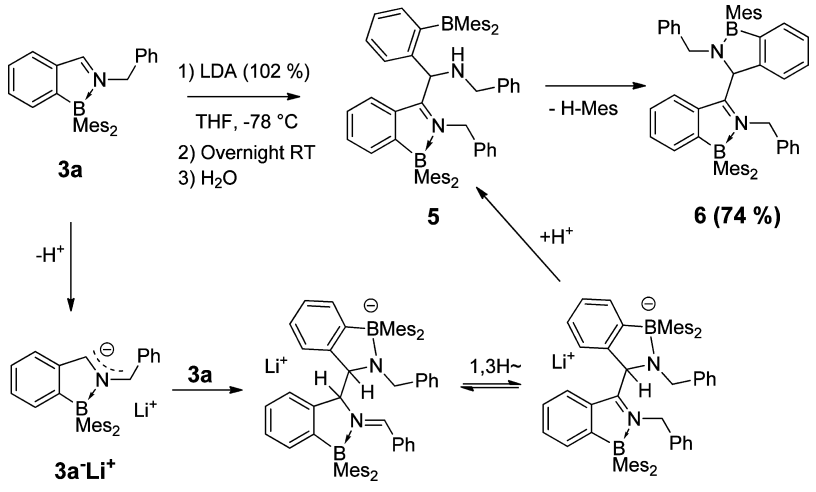
Table 3. Reaction Conditions and Isolated Yields for the Synthesis of Compound 6 from 3a as Starting Material

solvent/time, h/ temp, °C	base	electrophile (E^+)	product	yield, %
THF/1/−78	LDA	H_2O	**6**	74
THF/1/−78	LDA	*t*BuCOCl	**6**	16
THF/1/−78	LHMDS[a]	H_2O	*b*	
THF/1/−78	KO^{t}Bu	H_2O	**6**	*c*
THF/1/50	KO^{t}Bu	H_2O	*d*	*c*

[a]Lithium hexamethyldisilazide (LHMDS). [b]Only starting material could be obtained. [c]Could not be purified/yield not determined. [d]A complex mixture was obtained.

As the spectroscopic and crystallographic data indicate, compound **6** unexpectedly adopts a dimeric structure.[29] The proton NMR spectrum of **6** shows the characteristic signal for the CH_2 group of the saturated B/N heterocycle as a singlet at 4.44 ppm (Figure 3). At 4.63 ppm the methine group shows a resonance. The second methylene group splits into two doublets (4.92/5.73 ppm). The ^{11}B NMR shows two resonances at 6.21 ppm (sharp, *B*Mes_2) and 46.09 (broad singlet, *B*Mes). The ^{13}C

Scheme 3. Formation of Compound 6 after Deprotonation of 3a and Reaction with Water: (Upper Line) Overall Conversion; (Lower Line) Suggested Mechanism)



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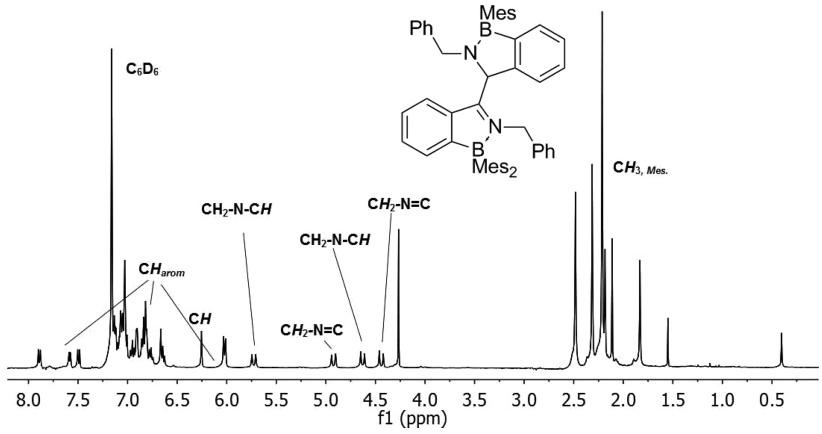

Figure 3. ^{1}H NMR spectrum of compound **6**.

NMR resonance of the iminic carbon is found at 178.7 ppm. Compound **6** is nonfluorescent.

Figure 4 displays the solid-state structure of **6**. The B−N bond length amounts to 1.673(2) Å for B(1)−N(1) and 1.408(2) Å for

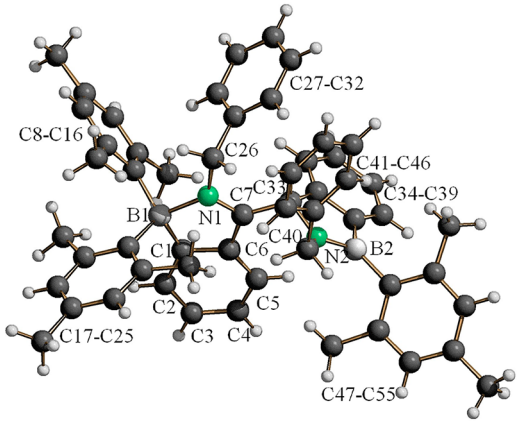

Figure 4. Molecular structure of compound **6** in the solid state (Schakal plot).

N(2)−B(2), respectively. In addition, the C−N bond distances within both B/N heterocycles vary significantly: C(7)−N(1) amounts to 1.310(2) Å, whereas the length of C(33)−N(2) is measured to be 1.479(2) Å. Compound **6** has tetracoordinated (B/N heterocycle, left) and tricoordinated boron centers (right) (Figure 3).

We were also able to characterize the structure of the labile compound **5** (Figure 5). **5** is suggested to be an intermediate of the dimerization of **3a** to give **6** by elimination of mesitylene (compare Scheme 3). Although we were not able to obtain satisfactory mass and NMR spectra for full characterization of intermediate **5**, we could identify characteristic peaks for **5** in the proton NMR spectra, which allowed us to follow the progress of the reaction from **3e** over **5** to form **6**. The recorded spectra indicate the formation of **5** within a few minutes after addition of the base to the solution of **3a**. After 1 h compound **5** was completely converted to **6**. Furthermore, after immediate quenching (10−15 min after the complete addition of base) of the reaction mixture of **3a** with water and recrystallization of the crude product in the cold, we were able to obtain a few crystals of **5** suitable for XRD analysis (Figure 5). Possibly, the conversion from **5** to **6** proceeds slowly in the solid state but quickly in solution. Characteristic bond lengths amount to 1.297 Å for C═

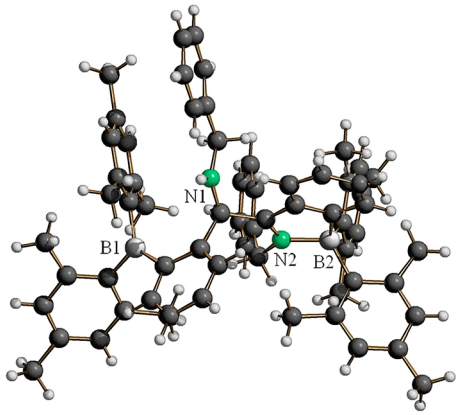

Figure 5. Molecular structure of compound **5** in the solid state (Schakal plot).

N and 1.639 Å for B→N in the unsaturated ring system and to 1.460 Å for the respective CH−NH bond in the open-chain boron- and nitrogen-containing part.

We suggest the electrophilic addition of **3a** to the lithium compound **3a**$^{-}$**Li**$^{+}$, a subsequent 1,3-proton shift, addition of a proton during the workup to give **5**, and final mesitylene elimination to form **6** as the mechanism for this unexpected dimerization (Scheme 3, lower line).

In experiments where different electrophiles such as *t*BuCOCl, benzyl bromide, methyl iodide, and silyl chlorides (as used in the case of **3e**) were added to the reaction mixture containing **3a**$^{-}$**Li**$^{+}$, these added electrophiles were not incorporated into the respective products (Scheme 3); even then, shorter reaction times, different solvents (hexanes, toluene, 1,4-dioxane), high dilution, and excess electrophile (up to 10 equiv) were used. In all cases the formation of compound **6** dominated and substituted compounds could only be detected in traces (ESI MS). We also tested compounds **3b−d** under these conditions. In all cases the reaction proceeded significantly more slowly, but we were not able to isolate any further derivatives.

Mechanistic Investigation/Quantum Chemical Calculations. The mechanisms for the reaction of compound **3e** to give **4a** and for the dimerization reaction of **3a** leading to **5** and **6** were also investigated by quantum chemical calculations at the SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d) level of theory using the program package GAUSSIAN 09[30] (see also ref 19). In general, the relative energies obtained at this level of theory are

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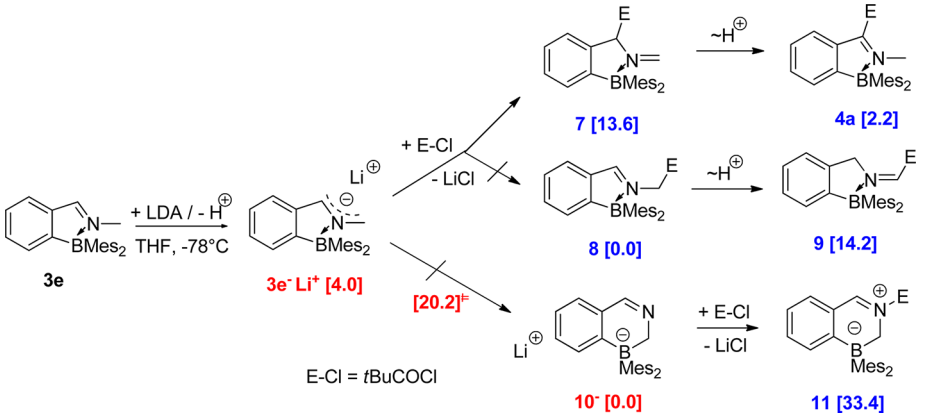
Scheme 4. Proposed Mechanism for the Formation of the α-Keto Imine 4a by Deprotonation of 3e and Subsequent Addition of Pivaloyl Chloride as Electrophile[a]



[a]For the 3D structure of $3e^-Li^+$ see Figure 6. Relative energies (kcal/mol) are given for the anions (red, without lithium cation) and for the neutral products (blue), respectively (SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)).

in good agreement with those from M062x/6-31G(d) optimizations.[31]

*Deprotonation of **3e** and Subsequent Reactions with Electrophiles.* In principle, the deprotonation reaction of **3e** may lead to the formation of two different ring systems, either to the five-membered 2-azaallyllithium compound $3e^-Li^+$ or to the six-membered ring system 10^-Li^+ (Scheme 4). Surprisingly, from the calculated total energies of the anions (without the lithium counterion) the six-membered anion 10^- is favored by 4.0 kcal/mol over $3e^-$. Thus, the exclusive experimental finding of derivatives **4** with a five-membered heterocycle is not in accord with these calculated thermodynamic data. Obviously, the cleavage of the N–B dative interaction by opening the five-membered ring of **3** during the deprotonation is kinetically disfavored under the reaction conditions (THF, −78 °C), thus leaving the five-membered-ring system unchanged. This is supported by quantum chemical calculations for the conversion of $3e^-$ to 10^- involving the cleavage of the Lewis acid–base interaction in $3e^-$, which affords an activation energy of 20.2 kcal/mol. Similarly, the experimentally observed regioselective formation of the α-keto imine **4a** cannot be explained by thermodynamic data. According to our calculations, the product **8**, resulting from the electrophilic attack of the pivaloyl chloride at the exoposition of the 2-azaallyl anion $3e^-Li^+$, is significantly lower in energy in comparison to the product resulting from attack at the endocyclic position of the anion (7^-). These data suggest a significant influence of the lithium counterion on the course of this reaction step in terms of kinetic control. Quantum chemical calculations of the lithiated species $3e^-Li^+$ show that the lowest-energy structure is characterized by the close proximity of the lithium cation to the endocyclic position position of the 2-azaallyl anion and to the center of one of the two mesityl rings, which is significantly bent toward the lithium cation (Figure 6 and the Supporting Information). In this way a type of pocket is formed (template) which in the course of the reaction is filled by the approaching electrophile. The NBO charges are significantly higher at the endocyclic carbon atom of the 2-azaallyl subunit (−0.381) in comparison to that at the exocyclic 2-azaallyl carbon atom (−0.182). The HOMO of $3e^-Li^+$ is characterized by a significantly larger π-orbital coefficient at the benzylic 1-position of the 1-phenyl-2-azaallyl subunit in comparison to that of the terminal CH_2– moiety at the 3-position (see the Supporting Information). Thus, both the structural features and the quantum chemical results suggest a strong directing influence of the lithium cation toward a regioselective electrophilic attack at the endocyclic position. This is in line with the experimental outcome of the reaction. The final proton shift from **7** to give **4a** is a result of thermodynamic control, as seen in Scheme 4.

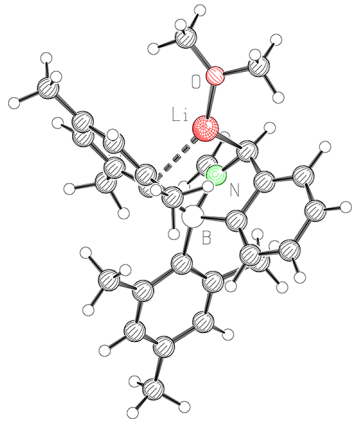


Figure 6. Calculated structure of the compound $3e^-Li^+·Me_2O$, indicating the lithium mesityl interaction (dotted line, 2.23 Å). The Li–CH(N) distance amounts to 2.13 Å.

*Base-Promoted Dimerization of Compound **3a**.* The unexpected formation of the dimerization products **5** and **6** may be explained in a similar way (see Scheme 3). Similarly to $3e^-Li^+$, the lithiated benzyl-substituted species $3a^-Li^+$ may react in a regioselective manner at the nucleophilic endo carbon atom of the 2-azaallyl moiety. However, here the reaction takes place exclusively with its neutral precursor molecule **3a**, which acts as an electrophile. In this case, the additional phenyl group (in comparison to **3e**) seems to contribute to the selectivity with respect to the electrophile. We assume that **3a** may adopt a favorable dimeric aggregate in solution, consisting of the deprotonated form $3a^-Li^+$ and **3a** itself, based again on the template effect exerted by the lithium ion, which leads then to the observed dimer **5**. Quantum chemical calculations predict that the base-catalyzed dimerization of **3a** to give **5** is exothermic by −14.6 kcal/mol (SCS-MP2; −7.0 kcal/mol at B3LYP/6-31G(d)/D3).[32] The formation of the isolated final product **6** from **5** is also highly exothermic (by −20.9 kcal/mol at SCS-MP2, −25.4 kcal/mol at B3LYP/6-31G(d)/D3; Scheme 3).

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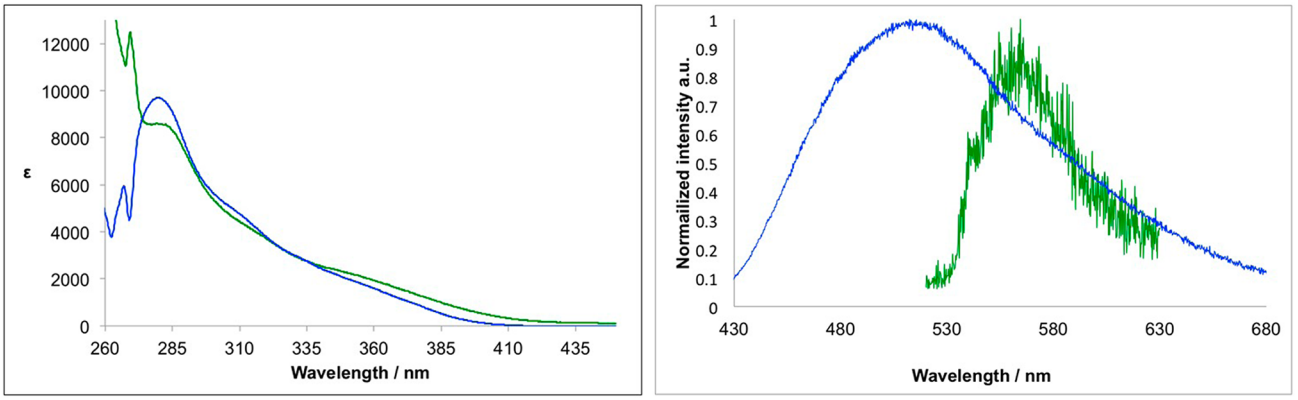

Figure 7. UV−vis (left) and fluorescence spectra (right) of **3e** (blue) and **4a** (green) (solvent dichloromethane).

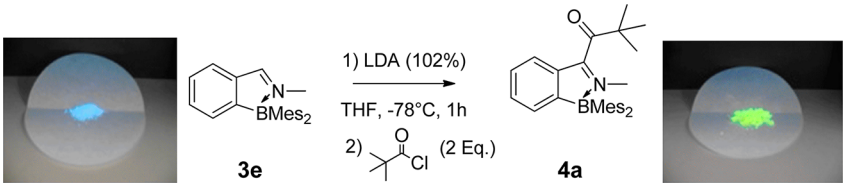

Figure 8. Change in the solid state photophysical properties of compound **3e** by functionalization to **4a** (UV hand lamp, 360 nm).

Influence of the Substitution Pattern on the Photophysical Properties. After deprotonation of **3e** and reaction with electrophiles, changes in the photophysical properties of the compounds were observed (Figure 7). For example, while the UV−vis spectrum of **3e**, dissolved in dichloromethane, displays absorptions at 265 and 279 nm and a shoulder at 307 nm (Figure 7, left), the acylated compound **4a** shows absorptions at 269 and 279 nm as well as a shoulder at 345 nm. In the fluorescence spectra (Figure 7, right, CH_2Cl_2, ~2.5×10^{-5} mol/L) compound **3e** shows an emission maximum at 512 nm ($\Phi_f(CH_2Cl_2) = 0.11$), whereas **4a** emits (weakly) at 561 nm (~2.5×10^{-5} mol/L). Thus, by this type of functionalization the emission maximum was red-shifted by ~50 nm. Similarly, in the solid state **3e** shows a blue fluorescence, while the acylated product **4a** emits a green to yellow fluorescence (irradiation at 360 nm, solid-state fluorescence not quantified, Figure 8). These preliminary photophysical studies underline the utility of these base-promoted functionalization reactions. Introducing further photophysically active or activating groups by such reactions might broaden the library of B/N heterocyclic compounds in the future.

Furthermore, compounds **3** show upon irradiation at 365 nm the formation of a second species in low concentrations, which could be observed by UV measurements. For example, the colorless compound **3a** changes its color upon irradiation at a wavelength of 365 nm to deep purple (weak absorption at 534 nm using a small scan window and fast scan rate); this color quickly fades after switching off the light source without heating. Therefore, we were not able to detect the photoproduct by NMR. This process could be repeated several times. In accordance with the very similar behaviors of structurally closely related compounds, we interpret this observation by photochromic switching, as extensively investigated by Wang[33] and coworkers. This photochromic reaction is not observed for compound **4a**.

CONCLUSION

Herein we report the synthesis and functionalization of various 2-borylbenzaldimines **3**. The functionalization reaction was studied using compound **3e** as the starting material. Thus, deprotonation with LDA and subsequent treatment with electrophiles in THF gave regioselectively functionalized compounds **4**, which show as an interesting photophysical property a substantial red-shifted emission. Compounds **3** display upon irradiation a reversible formation of a second species in low concentration, which may be interpreted in terms of photochromic switching, whereas **4a** does not show this photochemical phenomenon. In the case of compound **3a** dimer **6** was unexpectedly formed upon deprotonation via the intermediate species **5.** The unique dimeric compound **6** contains two B/N heterocyclic systems with tri- and tetravalent boron atoms. We have shown in this study that the mild functionalization reaction reported here is suitable even for sensitive compounds such as the B/N donor−acceptor complexes **3**, and it allows the modification of the photophysical properties of this important class of B/N heterocycles. We expect that this method might be a valuable contribution for ongoing studies in this research field.

EXPERIMENTAL SECTION

Melting points are uncorrected. All signals in the ^1H NMR and ^{13}C spectra were assigned on the basis of relative intensities, coupling constants, and GCOSY, GHSQC, and GHMBC experiments. Mass spectra (HRMS (ESI)) were recorded on a microTOF using electron spray ionization.

General Procedure for the Synthesis of [1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene]amines 3. A Schlenk flask was equipped with MS 4 Å, and a solution of compound **1**, dissolved in dry CH_2Cl_2, was transferred into the flask. Subsequently, the amine **2** was added pure or dissolved in dry CH_2Cl_2. After it was stirred at room temperature for 18 h, the mixture was filtered through a pad of Celite, which was washed with CH_2Cl_2 (3 × 30 mL). The solvent was removed in vacuo, and either the excess amine was removed by distillation or the compound was purified by recycling GPC or recrystallization.

Benzyl[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]-amine (3a). A 0.75 g portion (2.12 mmol) of **1** was dissolved in 50 mL

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of dry CH_2Cl_2. Subsequently, 0.23 mL (2.12 mmol) of benzylamine was added. The crude product was purified by washing with hexanes to give 0.84 g (1.90 mmol, 90%) of **3a** as a colorless solid. To obtain single crystals, the compound was recrystallized from CH_2Cl_2. Mp: 216 °C. IR (neat): $\tilde{\nu}$ 2914 cm^{-1} (w), 2357 (w), 2340 (w), 2226 (w), 2170 (w), 1607 (s), 1551 (w), 1443 (m), 1412 (m), 1375 (m), 1240 (m), 1219 (s), 1202 (m), 1175 (m), 1153 (m), 1115 (m), 1097 (m), 1070 (m), 1030 (m), 1022 (m). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) 282 nm (35460 cm^{-1}, 11319 M^{-1} cm^{-1}), 336 (sh, 28490 cm^{-1}, 2747 $M^{-1}.cm^{-1}$). Fluorescence (CH_2Cl_2, 1.5 × 10^{-5} mol/L): λ_{em} 522 nm ($\tilde{\nu}$ 19157 cm^{-1}), λ_{exc} 350 nm, $\Phi_f(CH_2Cl_2)$ = 0.13. ^{1}H NMR (C_6D_6, 300.13 MHz): δ 1.68 (bs, 3H), 2.00 (bs, 3H), 2.26 (s, 6H), 2.35 (bs, 3H), 2.51 (bs, 3H), 4.81−5.00 (m, 2H), 6.57−6.60 (m, 2H), 6.72 (bs, 1H), 6.86 (bs, 1H), 6.85−6.87 (m, 2H), 6.94−6.98 (m, 5H), 7.01−7.07 (m, 1H), 7.70 (s, 1H), 7.86 (d, 1H, ^3J = 6.0 Hz) ppm. ^{13}C NMR (C_6D_6, 75.48 MHz): δ 21.0, 23.0, 26.1, 26.2, 27.0, 55.12, 125.0, 125.8, 128.6, 129.3, 130.1, 130.4, 130.9, 131.1, 131.3, 132.3, 133.3, 135.1, 135.4, 136.9, 167.4 ppm. ^{11}B NMR (C_6D_6, 96.29 MHz): δ 6.46 ppm. HRMS (ESI): calcd for $C_{32}H_{34}BNH$ 444.2858, found 444.2870. X-ray crystal structure data of **3a** can be found in the Supporting Information.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene](4-chlorobenzyl)amine (3b). A 0.14 g portion (1.00 mmol) of 4-chlorobenzylamine dissolved in 50 mL of dry CH_2Cl_2 was added to a solution of 0.35 g (1.00 mmol) of **1** in 50 mL of dry CH_2Cl_2. Compound **3b** was purified by washing with pentane to give 0.17 g(0.37 mmol, 37%) of **3b** as a colorless solid. Mp: 229 °C. IR (neat): $\tilde{\nu}$ 3053 cm^{-1} (w), 3021 (w), 2972 (m), 2955 (m), 2922 (m), 2866 (w), 1609 (s), 1551 (m), 1491 (m), 1468 (m), 1441 (s), 1408 (m), 1371 (s), 1321 (m), 1310 (m), 1294 (m), 1281 (m), 1265 (m), 1221 (s), 1188 (w), 1165 (m), 1138 (m), 1107 (m), 1096 (s), 1061 (w), 1028 (s), 1015 (vs). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.61 (bs, 3H), 1.94 (bs, 3H), 2.24 (s, 6H), 2.31 (bs, 3H), 2.49 (bs, 3H), 4.50 (d, ^2J = 16.0 Hz, 1H), 4.74 (d, ^2J = 16.0 Hz, 1H), 6.20−6.23 (m, 2H), 6.72 (bs, 1H), 6.77 (bs, 1H), 6.87−6.91 (m, 3H), 6.93 (bs, 1H), 6.97−7.02 (m, 2H), 7.05 (td, ^3J = 8.0 Hz, ^4J = 3.0 Hz, 1H), 7.55 (s, 1H), 7.86 (d, ^3J = 6.0 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.61 MHz): δ 21.0, 22.8, 23.0, 26.0, 26.2, 27.0, 54.3, 125.2, 125.8, 128.4, 129.3, 130.1, 131.0, 131.1, 131.4, 131.5, 132.5, 133.4, 133.9, 134.6, 135.2, 136.7, 136.8, 141.0, 141.8, 144.0, 167.8 ppm. ^{11}B NMR (C_6D_6, 96.29 MHz): δ 6.79 ppm. HRMS (ESI): calcd for $C_{32}H_{33}BClNNa$ 500.2287, found 500.2265. Anal. Calcd for $C_{32}H_{33}BClN$ (477.88): C, 80.43; H, 6.96; N, 2.93. Found: C, 80.31; H, 6.97; N, 2.70.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene](4-methoxybenzyl)amine (3c). A 0.35 g portion (1.00 mmol) of compound **1** was dissolved in 100 mL of dry CH_2Cl_2. Then, 0.13 mL (1.00 mmol) of 4-methoxybenzylamine was added. The product was purified by washing with pentane to give 0.25 g (0.52 mmol, 52%) of **3c** as a colorless solid. Single crystals could be obtained by recrystallization from CH_2Cl_2. Mp: 209 °C. IR (neat): $\tilde{\nu}$ 3046 cm^{-1} (w), 3019 (m), 3005 (w), 2994 (w), 2972 (m), 2955 (m), 2913 (m), 2866 (w), 2841 (w), 1609 (s), 1584 (w), 1551 (m), 1512 (s), 1491 (w), 1460 (m), 1441 (s), 1412 (m), 1371 (m), 1319 (m), 1302 (m), 1281 (m), 1256 (vs), 1217 (s), 1182 (m), 1175 (s), 1165 (m), 1138 (m), 1111 (m), 1094 (w), 1072 (w), 1038 (m), 1026 (s), 1015 (s). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.71 (bs, 3H), 2.03 (bs, 3H), 2.27 (bs, 6H), 2.37 (bs, 3H), 2.52 (bs, 3H), 3.21 (s, 3H), 4.744.88 (m, 2H), 6.53−6.61 (m, 4H), 6.73 (bs, 1H), 6.85 (bs, 1H), 6.86−6.90 (m, 1H), 6.95−6.96 (m, 1H), 6.99 (bs, 2H), 7.06 (td, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.80 (s, 1H), 7.88 (d, ^3J = 7.6 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.61 MHz): δ 21.0, 22.9, 26.1, 26.2, 27.0, 54.6, 54.8, 114.8, 125.1, 125.7, 127.2 (*C*), 128.4, 130.1, 130.9, 131.1, 131.4, 131.7, 132.2, 135.1, 136.9, 137.0, 141.0, 141.8, 144.1, 160.2, 167.2 ppm. ^{11}B NMR (C_6D_6, 64.21 MHz): δ 5.05 ppm. HRMS (ESI): calcd for $C_{33}H_{36}BNONa$ 496.2788, found 496.2797. Anal. Calcd for $C_{33}H_{36}BNO$ (473.46): C, 83.71; H, 7.66; N, 2.96. Found: C, 83.60; H, 7.48; N, 2.71.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene](2,4-dimethoxybenzyl)amine (3d). A 0.35 g portion (1.00 mmol) of **1** was dissolved in 100 mL of dry CH_2Cl_2. Subsequently, 0.15 g (1.02 mmol) of 2,4-dimethoxybenzylamine was added. Recrystallization from CH_2Cl_2 gave 0.31 g (0.62 mmol, 62%) of **3d** as colorless crystals. Mp: 256 °C. IR (neat): $\tilde{\nu}$ 3019 cm^{-1} (vw), 2999 (w), 2974 (m), 2943 (m), 2928 (m), 2882 (vw), 2866 (w), 2837 (vw), 2361 (w), 2342 (vw), 2330 (vw), 1611 (vs), 1585 (vs), 1555 (m), 1506 (vs), 1468 (vs), 1458 (vs), 1449 (vs), 1439 (vs), 1420 (m), 1410 (m), 1379 (s), 1327 (m), 1285 (vs), 1267 (vs), 1240 (m), 1209 (vs), 1157 (vs), 1134 (vs), 1090 (vw), 1074 (vw), 1036 (vs), 1022 (vs). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 1.40 (bs, 3H), 1.98 (bs, 3H), 2.04 (bs, 3H), 2.14 (bs, 3H), 2.17 (bs, 3H), 2.23 (bs, 3H), 3.68 (s, 3H), 3.81 (s, 3H), 4.63 (d, ^2J = 16.2 Hz, 1H), 5.03 (d, ^2J = 16.2 Hz, 1H), 6.43−6.43 (m, 1H), 6.50 (d, ^3J = 2.4 Hz, 1H., 6.53 (bs, 1H), 6.64 (bs, 1H), 6.72 (d, ^3J = 8.1 Hz, 1H), 6.76 (bs, 1H), 6.79 (bs, 1H), 7.16 (td, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 1H), 7.29 (td, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.52 (d, ^3J = 7.5 Hz, 1H), 7.61 (d, ^3J = 7.5 Hz, 1H), 8.00 (s, 1H) ppm. ^{13}C NMR (CD_2Cl_2, 75.47 MHz): δ 20.7, 20.9, 22.4, 25.7, 26.2, 50.5, 55.5, 55.8, 98.8, 105.2, 115.2, 125.1, 126.1, 129.3, 129.6, 130.2, 130.5, 131.8, 132.9, 137.3, 159.5, 162.2, 167.1 ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz): δ 5.34 ppm. HRMS (ESI): calcd for $C_{34}H_{38}BNNaO_2$ 526.2888, found 526.2893. X-ray crystal structure data of **3d** can be found in the Supporting Information.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene]methylamine (3e). A 2.36 g portion (6.65 mmol) of compound **1** was dissolved in 100 mL of dry CH_2Cl_2. Then, 0.80 mL (7.32 mmol) of methylamine (40% in MeOH) was added with stirring. The crude product was washed with pentane. Crystals could be obtained by recrystallization from CH_2Cl_2 to give 2.17 g (5.90 mmol, 70%) of **3e** as colorless crystals. Mp: 230 °C. IR (neat): $\tilde{\nu}$ 3057 cm^{-1} (vw), 3007 (w), 2990 (w), 2965 (m), 2914 (m), 2866 (w), 2729 (vw), 2361 (w), 2342 (w), 2334 (w), 2326 (w), 1638 (vw), 1614 (s), 1603 (m), 1551 (m), 1506 (w), 1468 (m), 1447 (s), 1406 (m), 1379 (m), 1371 (s), 1310 (w), 1283 (w), 1263 (w), 1229 (m), 1200 (w), 1186 (w), 1163 (m), 1138 (s), 1117 (w), 1099 (w), 1070 (w), 1045 (m), 1020 (m), 1013 (m). UV/vis (CH_2Cl_2): λ_{abs} 280 nm ($\tilde{\nu}$ 35714 cm^{-1}, ε = 9702 M^{-1} cm^{-1}), 308 (sh, 32467 cm^{-1}, 4909 M^{-1} cm^{-1}), 354 (sh, 28248 cm^{-1}, 1834 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2, 2.5 × 10^{-5} mol/L): λ_{em} 512 nm ($\tilde{\nu}$ 19531 cm^{-1}), λ_{exc} 280 nm, $\Phi_f(CH_2Cl_2)$ = 0.11. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.72 (bs, 6H), 2.23 (bs, 12H), 2.83 (s, 3H), 6.75−6.94 (m, 5H), 6.97 (td, ^3J = 7.2 Hz, ^4J = 0.8 Hz, 1H), 7.07 (td, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.18 (s, 1H), 7.82 (d, ^3J = 8.0 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.61 MHz): δ 21.0, 25.8, 40.5, 125.1, 125.2, 128.3, 130.3, 131.5, 132.0, 136.9, 141.3, 169.0 ppm. ^{11}B NMR (C_6D_6, 96.29 MHz): δ 5.00 ppm. HRMS (ESI): calcd for $C_{26}H_{30}BNNa$ 390.2368, found 390.2360. Anal. Calcd for $C_{26}H_{30}BN$ (367.33): C, 85.01; H, 8.23; N 3.81. Found: C, 85.05; H, 8.38; N, 3.72. X-ray crystal structure data of **3e** can be found in the Supporting Information.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene](2,2-dimethyl-propyl)amine (3f). A 1.67 g portion (4.73 mmol) of compound **1** was dissolved in 25 mL of dry CH_2Cl_2. Then, 0.55 mL (4.82 mmol) of neopentylamine was added. The crude product was washed with pentane. Slightly yellow crystals were obtained by recrystallization from CH_2Cl_2. Yield: 1.13 g (2.67 mmol, 56%). Mp: 115 °C. IR (neat): $\tilde{\nu}$ 3024 cm^{-1} (vw), 2961 (s), 2918 (m), 2870 (w), 2359 (w), 2340 (w), 1609 (vs), 1551 (s), 1470 (vs), 1447 (vs), 1404 (m), 1379 (m), 1373 (m), 1339 (m), 1308 (w), 1281 (w), 1263 (m), 1234 (m), 1225 (m), 1204 (w), 1194 (m), 1163 (w), 1144 (m), 1105 (m), 1080 (s), 1059 (s), 1045 (s), 1030 (s), 1015 (vs). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 0.45 (s, 9H), 1.75 (bs, 3H), 1.94 (bs, 3H), 2.20 (bs, 3H), 2.22 (bs, 3H), 2.44 (bs, 3H), 3.40−3.45 (m, 1H), 3.87−3.92 (m, 1H), 6.65 (bs, 1H), 6.74 (bs, 1H), 6.89 (bs, 1H), 6.95 (bs, 1H), 6.99 (td, ^3J = 7.2 Hz, ^4J = 0.9 Hz, 1H), 7.10 (td, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.29 (d, ^3J = 7.5 Hz, 1H), 7.90 (d, ^3J = 6.0 Hz, 1H), 8.03 (s, 1H) ppm. ^{13}C NMR (C_6D_6, 75.47 MHz): δ 21.0, 21.0, 23.1, 25.9, 27.6, 28.5, 33.4, 62.1, 125.0, 125.8, 127.7, 128.2, 128.4, 130.0, 130.2, 130.4, 131.3, 131.5, 132.5, 133.1, 135.1, 136.6, 136.7, 141.3, 142.5, 143.8, 168.7 ppm. ^{11}B NMR (C_6D_6, 96.29 MHz): δ 5.96 ppm. HRMS (ESI): calcd for $C_{30}H_{39}BN$ 424.3170, found 424.3172. X-ray crystal structure data of **3f** can be found in the Supporting Information.

Allyl[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]amine (3g). A 0.38 g (1.07 mmol) portion of compound **1** was dissolved in 100 mL of dry CH_2Cl_2. Then, 0.10 mL (1.33 mmol) of allylamine was added. To purify the crude product, the solid was washed with pentane. Colorless crystals were obtained by recrystallization from diethyl ether. Yield: 0.25 g (0.62 mmol, 58%). Mp: 143 °C. IR (neat): $\tilde{\nu}$ 3011 cm^{-1} (m), 2967 (s), 2959 (s), 2924 (s), 2884 (m), 2870 (m), 2862 (m), 1607

(vs), 1549 (vs), 1470 (vs), 1449 (vs), 1441 (vs), 1414 (s), 1377 (vs), 1321 (m), 1310 (m), 1298 (m), 1283 (w), 1263 (m), 1244 (m), 1234 (m), 1215 (s), 1163 (w), 1134 (vs), 1105 (m), 1088 (m), 1074 (m), 1047 (vs), 1022 (vs). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 1.67 (bs, 3H), 1.84 (bs, 3H), 2.22 (bs, 9H), 2.48 (bs, 3H), 4.01−4.22 (m, 2H), 4.60−4.71 (m, 2H), 4.93−5.06 (m, 1H), 6.74 (bs, 2H), 6.94 (bs, 2H), 6.97 (td, ^3J = 6.3 Hz, ^4J = 0.9 Hz, 1H), 7.08 (td, ^3J = 6.0 Hz, ^4J = 1.2 Hz, 1H), 7.22 (d, ^3J = 7.2 Hz, 1H), 7.63 (s, 1H), 7.88 (d, ^3J = 7.8 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 75.47 MHz): δ 21.0, 22.7, 26.0, 27.1, 54.5, 120.7, 125.1, 125.7, 128.4, 130.1, 130.9, 131.4, 132.3, 133.2, 134.8, 137.1, 141.4, 143.7, 167.4 ppm. ^{11}B NMR (C_6D_6, 96.29 MHz): δ 5.41 ppm. HRMS (ESI): calcd for $C_{28}H_{33}BN$ 394.2701, found 394.2708. Anal. Calcd for $C_{28}H_{32}BN$ (393.37): C, 85.49; H, 8.20; N 3.56. Found: C, 85.18; H, 8.23; N, 3.40. X-ray crystal structure data of **3g** can be found in the Supporting Information.

General Procedure for the Synthesis of Compounds 4. Compounds **3** were dissolved in THF and added slowly to a stirred solution of diisopropylamine and ^{n}BuLi at −78 °C. After 1 h the deeply colored mixture was quenched with an excess of electrophile. After 15 min the reaction mixture was warmed to ambient temperature and stirred for a further 1 h. Diethyl ether was added, and the organic phase was washed three times with water and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude products were purified by either recrystallization or column chromatography.

(*Z*)-1-[2-(Dimesitylboranyl)phenyl]-3,3-dimethyl-1-(methylimino)butan-2-one (4a). A 0.37 g portion (0.99 mmol) of compound **3e** in 20 mL of dry THF was added slowly to a stirred mixture of diisopropylamine (0.14 mL, 1.02 mmol) and ^{n}BuLi (0.64 mL, 1.02 mmol, 1.6 M in hexane). After 1 h at −78 °C, the reactive intermediates were quenched with 0.22 mL (2.00 mmol) of trimethylacetyl chloride. The crude product was purified by recrystallization from diethyl ether to give 0.32 g (0.71 mmol, 72%) of **4a** as colorless crystals. Mp: 174 °C. IR (neat): $\tilde{\nu}$ 2990 cm^{-1} (m), 2974 (m), 2955 (m), 2926 (m), 2872 (m), 1695 (s), 1603 (m), 1549(m), 1468 (s), 1445 (s), 1406 (m), 1398 (m), 1369 (m), 1362 (m), 1333 (s), 1310 (m), 1269 (m), 1233 (m), 1163 (m), 1148 (m), 1124 (m), 1036 (s), 1020 (m), 1001 (s). UV/vis (CH_2Cl_2): λ_{abs} 269 nm ($\tilde{\nu}$ 37175 cm^{-1}, ε = 12485 M^{-1} cm^{-1}), 279 nm (35894 cm^{-1}, 8602 M^{-1} cm^{-1}), 345 nm (sh, 29002 cm^{-1}, 2416 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2, 2.5 × 10^{-5} mol/L): λ_{em} 561 nm ($\tilde{\nu}$ 17813 cm^{-1}), λ_{exc} 269 nm. ^{1}H NMR (C_6D_6, 399.65 MHz): δ 0.88 (s, 9H), 1.96 (s, 6H), 2.21 (s, 9H), 2.44 (s, 3H), 2.91 (s, 3H), 6.64 (bs, 1H), 6.81−6.86 (m, 2H), 6.91−6.94 (m, 2H), 7.03 (t, ^3J = 7.2 Hz, 1H), 7.14−7.16 (m, 1H), 7.87 (d, ^3J = 7.6 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.40 MHz): δ 20.8, 22.6, 25.6, 25.8, 26.2, 28.0, 30.0, 37.6, 44.4, 124.8, 125.3, 130.2, 130.6, 130.7, 130.8, 131.9, 132.4, 133.7, 134.8, 136.1, 141.1, 175.3, 210.5 ppm. ^{11}B NMR (C_6D_6, 128.15 MHz): δ 5.07 ppm. HRMS (ESI): calcd for $C_{31}H_{38}BNONa$ 474.2939, found 474.2942. Anal. Calcd for $C_{31}H_{38}BNO$ (451.45): C, 82.47; H, 8.48; N 3.10. Found: C, 82.20; H, 8.57; N, 3.09. X-ray crystal structure data of **4a** can be found in the Supporting Information.

(*Z*)-2-[2-(Dimesitylboranyl)phenyl]-2-(methylimino)-1-phenylethanone (4b). A 0.37 g portion (1.00 mmol) of compound **3e** in 20 mL of dry THF was added slowly to a stirred mixture of diisopropylamine (0.14 mL, 1.01 mmol) and ^{n}BuLi (0.62 mL, 1.01 mmol, 1.6 M in hexane) in 50 mL of dry THF. After 1 h at −78 °C, the reactive intermediates were quenched with 0.24 mL (2.04 mmol) of benzoyl chloride. The crude product was purified by column chromatography and subsequent recrystallization from toluene to give 0.31 g (0.65 mmol, 65%) of **4b** as colorless crystals. R_f = 0.33, Al_2O_3, cyclohexane/ethyl actetate (40/1). Mp: 215 °C,. IR (neat): $\tilde{\nu}$ 2961 cm^{-1} (s), 2930 (s), 2359 (w), 2342 (m), 1665 (vs), 1603 (s), 1595 (s), 1578 (s), 1516 (s), 1497 (s), 1470 (s), 1447 (s), 1441 (s), 1406 (s), 1371 (s), 1356 (s), 1342 (s), 1317 (s), 1240 (vs), 1179 (s), 1146 (s), 1107 (s), 1022 (s), 991 (s), 899 (s), 854 (s), 845 (s), 822 (s), 746 (vs), 735 (vs), 714 (s), 698 (vs), 681 (s). ^{1}H NMR (C_6D_6, 300.13 MHz): δ 2.23 (bs, 18H), 2.98 (s, 6H), 6.73−6.78 (m, 1H), 6.85−6.90 (m, 5H), 6.94−7.08 (m, 3H), 7.10−7.14 (m, 1H), 7.78 (m, 2H), 7.92 (d, ^3J = 7.5 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 75.48 MHz): δ 21.0, 27.2, 37.1, 125.1, 125.7, 128.3, 129.4, 129.6, 130.6, 131.8, 132.6, 134.3, 134.8, 135.5, 136.7, 173.8, 192.1 ppm. ^{11}B NMR (C_6D_6, 100.61 MHz): δ 7.22 ppm. HRMS (ESI): calcd for $C_{33}H_{34}BNONa$ 494.2626, found 494.2602. X-ray crystal structure data of **4b** can be found in the Supporting Information.

(*Z*)-*N*-[(2-(Dimesitylboranyl)phenyl)(trimethylsilyl)methylene]methanamine (4c). A 0.48 g portion (1.31 mmol) of compound **3e** was dissolved in 20 mL of dry THF and added slowly to a stirred mixture of diisopropylamine (0.22 mL, 1.58 mmol) and ^{n}BuLi (0.98 mL, 1.58 mmol, 1.6 M in hexane) in 50 mL of dry THF. After 1 h at −78 °C, the reactive intermediates were trapped with 0.33 mL (2.62 mmol) of trimethylsilyl chloride. The crude product was purified by column chromatography and recycling GPC (toluene) to give 0.32 g (0.73 mmol, 56%) of **4c** as a yellow solid. R_f = 0.21, Al_2O_3, cyclohexane (100%) Mp: 150 °C,. IR (neat): $\tilde{\nu}$ 3059 cm^{-1} (w), 3017 (w), 2965 (m), 2949 (m), 2920 (s), 2855 (m), 1603 (m), 1591 (m), 1547 (w), 1526 (m), 1468 (s), 1447 (vs), 1414 (m), 1400 (m), 1379 (m), 1346 (w), 1308 (m), 1252 (vs), 1234 (m), 1209 (w), 1200 (w), 1184 (w), 1163 (m), 1152 (m), 1099 (w), 1074 (w), 1053 (m), 1030 (m), 1018 (m), 974 (w), 962 (w), 943 (w), 930 m), 845 (vs), 822 (vs), 804 (s), 785 (vs), 766 (s), 743 (vs), 718 (vs), 692 (s), 673 (m), 664 (w), 644 (s), 629 (m), 623 (m). ^{1}H NMR (C_6D_6, 399.65 MHz): δ 0.08 (s, 9H), 1.7 (s, 3H), 2.23 (s, 3H), 3.23 (s, 3H), 6.77 (bs, 4H), 6.94−7.02 (m, 1H), 7.05−7.11 (m, 1H), 7.66 (d, ^3J = 8.0 Hz, 1H), 7.95 (d, ^3J = 8.0 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.40 MHz): δ 0.2, 20.9, 30.1, 40.1, 124.5, 125.7,126.3, 128.4, 128.6, 129.3, 130.4, 130.9, 131.2, 141.6, 143.7, 190.2 ppm. ^{11}B NMR (C_6D_6, 128.15 MHz): δ 4.89 ppm. ^{29}Si NMR (C_6D_6, 59.62 MHz): δ −5.58 ppm. HRMS (ESI): calcd for $C_{29}H_{38}BNSiNa$ 462.2764, found 462.2767. Anal. Calcd for $C_{29}H_{38}BNSi$ (439.52): C, 79.25; H, 8.71; N 3.19. Found: C, 79.12; H, 8.77; N, 2.99.

(*Z*)-*N*-[(2-(Dimesitylboranyl)phenyl)(triphenylsilyl)methylene]methanamine (4d). A 0.37 g portion (1.00 mmol) of compound **3e** dissolved in 20 mL of dry THF was prepared and added slowly to a stirred mixture of diisopropylamine (0.14 mL, 1.02 mmol) and ^{n}BuLi (0.64 mL, 1.02 mmol, 1.6 M in hexane) in 50 mL of dry THF. After 1 h at −78 °C, the reactive intermediates were trapped with 0.59 mL (2.00 mmol) of triphenylsilyl chloride in 20 mL of dry THF. The crude product was purified by recycling GPC (toluene) to give 0.36 g (0.58 mmol, 58%) of **4d** as a yellow solid. Mp: 229 °C,. IR (neat): $\tilde{\nu}$ 3026 cm^{-1} (w), 2974 (w), 2916 (w), 1526 (w), 1470 (w), 1447 (m), 1439 (m), 1414 (w), 1252 (s), 1150 (w), 1016 (w), 870 (w), 847 (vs), 820 (m), 785 (s), 766 (w), 743 (vs), 723 (vs), 700 (s), 692 (m), 681 (w), 667 (vs), 658 (w), 629 (w), 615 (w). ^{1}H NMR (C_6D_6, 399.65 MHz): δ 2.11 (bs, 6H), 2.26 (bs, 12H), 3.23 (s, 3H), 6.71 (t, ^3J = 7.2 Hz, 1H), 6.87 (bs, 4H), 6.96−7.03 (m, 1H), 7.05−7.15 (m, 9H), 7.25 (d, ^3J = 8.0 Hz, 1H), 7.56−7.58 (m, 6H), 7.93 (d, ^3J = 8.0 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.40 MHz): δ 20.9, 42.2, 124.6, 128.1, 128.3, 128.9, 130.5, 130.9, 130.9, 131.6, 132.1, 133.8, 136.4, 145.5, 185.9 ppm. ^{11}B NMR (C_6D_6, 128.15 MHz): δ 5.73 ppm. HRMS (ESI): calcd for $C_{44}H_{44}BNSiNa$ 648.3236, found 648.3236. Anal. Calcd for $C_{44}H_{44}BNSi$ (625.72): C, 84.46; H, 7.09; N 2.24. Found: C, 84.11; H, 6.93; N, 2.04.

Dimer 5. Although compound **5** could neither be isolated in pure form nor be fully characterized by spectroscopy, its structure in the solid state could be determined unambiguously. See the Supporting Information for details of the X-ray structure.

Dimer 6. A 0.22 g portion (0.50 mmol) of compound **3a** in 20 mL of dry THF was added slowly to a stirred mixture of diisopropylamine (0.07 mL, 0.51 mmol) and ^{n}BuLi (0.32 mL, 0.51 mmol, 1.6 M in hexane). After 1 h at −78 °C, the reactive intermediates were quenched with 10 mL of distilled H_2O. The crude product was purified by recycling GPC. Colorless single crystals were obtained by recrystallization from CH_2Cl_2 to give 0.14 g (0.37 mol, 74%) of **6**. Mp: 158 °C. IR (neat): $\tilde{\nu}$ 3026 cm^{-1} (w), 2974 (w), 2916 (w), 1526 (w), 1470 (w), 1447 (m), 1439 (m), 1414 (w), 1252 (s), 1150 (w), 1016 (w), 870 (w), 847 (vs), 820 (m), 785 (s), 766 (w), 743 (vs), 723 (vs), 700 (s), 692 (m), 681 (w), 667 (vs), 658 (w), 629 (w), 615 (w). ^{1}H NMR (C_6D_6, 399.65 MHz): δ 1.83 (bs, 3H), 2.11 (bs, 3H), 2.18 (bs, 3H), 2.21 (bs, 15H), 2.31 (bs, 6H), 2.48 (bs, 6H), 4.44 (d, ^2J = 16.4 Hz, 1H), 4.63 (d, ^2J = 15.6 Hz, 1H), 4.92 (d, ^2J = 16.4 Hz, 1H), 5.73 (d, ^2J = 15.6 Hz, 1H), 6.02 (d, ^3J = 7.6 Hz, 2H), 6.25 (s, 1H), 6.63−7.14 (m, 21H), 7.49 (d, ^3J = 8.0 Hz, 1H), 7.58 (d, ^3J = 6.4 Hz, 1H), 7.89 (d, ^3J = 7.6 Hz, 1H) ppm. ^{13}C NMR (C_6D_6, 100.40 MHz): δ 20.7, 20.9, 21.2, 21.3, 23.0, 23.4, 24.7, 25.7, 26.4, 27.9, 50.2, 54.8, 64.3, 123.1, 124.8, 125.7, 126.6, 126.8, 127.7, 127.8,

127.9, 128.4, 128.5, 128.6, 129.3, 129.4, 129.6, 130.4, 130.7, 131.5, 131.6, 132.0, 132.3, 135.3, 136.5, 137.7, 138.0, 138.6, 138.8, 140.5, 141.0, 141.2, 142.6, 142.9, 144.7, 146.6, 151.4, 178.7 ppm. ^{11}B NMR (C_6D_6, 128.15 MHz): δ 6.21 ppm (s), 46.09 (bs). HRMS (ESI): calcd for $C_{55}H_{56}B_2N_2Na$ 789.4522, found 789.4513. Anal. Calcd for $C_{55}H_{56}B_2N_2$ (766.67): C, 86.16; H, 7.36; N 3.65. Found: C, 85.87; H, 7.58; N, 3.20. X-ray crystal structure data of **6** can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving ^{1}H, ^{11}B, and ^{13}C NMR spectra for the new compounds, time-dependent spectra of NMR experiments, graphics of the crystal structures showing thermal ellipsoids with 50% probability, optimized Cartesian coordinates (B3LYP/6-31G(d) and SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE energies) for the calculated structures, details of TD-DFT calculations, Wiberg bond indices obtained from NBO calculations (B3LYP/6-31G(d)), and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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