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Betaine–Carbene Interconversions. From N-Ylides to Zwitterionic N-Heterocyclic Carbene–Borane Adducts

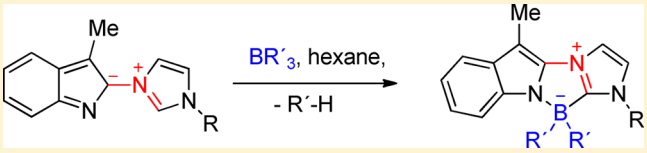
Nazar Pidlypnyi,[†] Jan C. Namyslo,[†] Martin H. H. Drafz,[†] Martin Nieger,[‡] and Andreas Schmidt[†,*]

[†]Institute of Organic Chemistry, Clausthal University of Technology, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld, Germany

[‡]Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

Supporting Information

ABSTRACT: In the presence of NBS 3-methylindole reacted with various imidazoles to give the (indol-2-yl)imidazolium salts **21a–f**, which were converted in aqueous solution into the 2-(imidazolium-3-yl)-3-methylindolates **22a–f** by base. These conjugated ylides—which represent a subclass of mesomeric betaines—are the exclusively detectable form in the NMR spectra taken in DMSO-d_6. A DFT calculation revealed that the betaine **22a** is −9.3 kJ/mol more stable than the tautomeric N-heterocyclic carbene **23a** and that the energy for the betaine–carbene interconversion is $\Delta G^{\ddagger}$ = 66.4 kJ/mol. The N-heterocyclic carbenes (3-methyl-indol-2-yl)imidazol-2-ylidenes, however, can be trapped by sulfur, triethylborane, and triphenylborane. Whereas the first trapping reaction yielded the expected imidazolethiones, the borates gave the first representatives of new zwitterionic borane adducts, imidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]indolium-11-ides **26a–h**. We performed DFT calculations on the structures of mesomeric betaine **22a**, the carbene **23a**, and the mechanisms of the borane adduct formation to **26a–h**, NMR spectroscopic investigations including ^{15}N, ^{7}Li, and ^{11}B NMR spectroscopy, and an X-ray single-crystal analysis of one of the borane adducts.



INTRODUCTION

Since pioneering work by Breslow,[1] Wanzlick,[2] and Öfele[3] and the isolation of the first stable carbenes by Bertrand[4] ((phosphine)(silyl)carbene) and Arduengo[5] (N-heterocyclic carbene (NHC)) the class of N-heterocyclic carbenes has developed remarkably. Among other motivations,[6] numerous structural variations have been performed aiming at enhancing the electron density at the carbene center and thus influencing the σ-donor capacity in catalytically active metal complexes. Figure 1 presents the isomers imidazol-2-ylidene **1** as a "classical" NHC,[7] imidazol-4-ylidene **2** as a member of the class of *abnormal* N-heterocyclic carbenes (*a*NHC)[8] and pyrazol-4-ylidene **3**. The latter has inter alia been described as structure **3A**, which was termed a *remote* N-heterocyclic carbene (*r*NHC)[9] or aromatic zwitterion.[10] Its representation as cyclic bent allene **3B**[11] or as dipolar electron-sextet structure **3C**[12] reflects the sensitivity of this compound toward substituent effects, which has been calculated in detail.[11,12] The term "mesoionic carbene" (MIC) has been suggested by Bertrand for certain *a*NHCs and *r*NHCs, because no reasonable canonical resonance form containing a carbene can be drawn.[13] In cyclic alkyl(amino)carbenes **4** (CAAC) a nitrogen is replaced by the strongly σ-donating carbon.[14] In contrast, the amino–phosphorus–ylide–carbenes **5**[15] and amino–sulfur–ylide carbenes **6**[16] possess ylides as partial structures.

Heterocyclic mesomeric betaines (MB) have constituted a classical subject of research to date. The first mesoion (1882),[17] mesomeric betaine (1891),[18] sydnone (1935),[19] classification

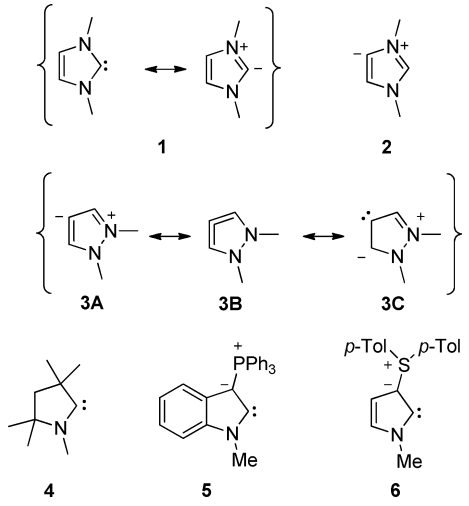


Figure 1. Distinct types of N-heterocyclic carbenes.

(1955),[20] and münchnone (1963)[21] are milestones in the development of this class of compounds. Mesomeric betaines are defined as neutral compounds which can exclusively be represented by dipolar canonical formulas in which the positive and negative charges are delocalized within a common π-electron system.[22] A comprehensive classification was recog-

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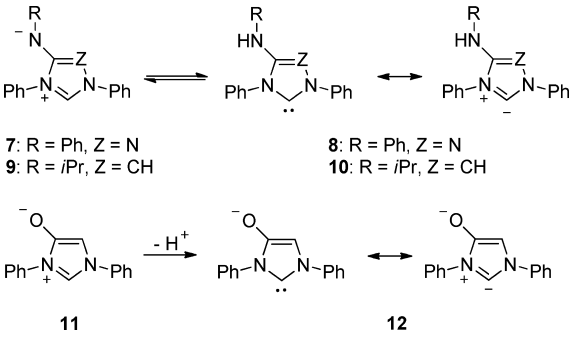
nized in 1985, and since then four distinct main classes of heterocyclic mesomeric betaines have been distinguished.[23] These are conjugated (CMB), cross-conjugated (CCMB), and pseudo-cross-conjugated mesomeric betaines (PCCMB), in addition to ylides which are closely related to CMB. Mesoionic compounds have been defined as five-membered representatives of CMB.[22] Numerous examples of 144 theoretically predicted type A and of 84 type B mesoionic compounds[23] have been described to date.

A review analyzing the relationship between the two classes of compounds, N-heterocyclic carbenes and mesomeric betaines, has been published, as far as the chemistry of pyrazoles and indazoles is concerned.[24] However, the relationship of the distinct classes of N-heterocyclic carbenes (especially NHC, *r*NHC, *a*NHC, and MIC) and mesomeric betaines (CMB, CCMB, PCCMB, ylides) with respect to structures, properties, and reactions has not been examined systematically to date. Results of a few scattered reports and some own thoughts on the structures are as follows. Nitrone **7** (Busch's reagent, a CMB, subclass mesoionic compounds) is in equilibrium with its N-heterocyclic carbene **8** (Scheme 1).

Scheme 1. Classical Mesoionic Compounds and Their Conversions into N-Heterocyclic Carbenes

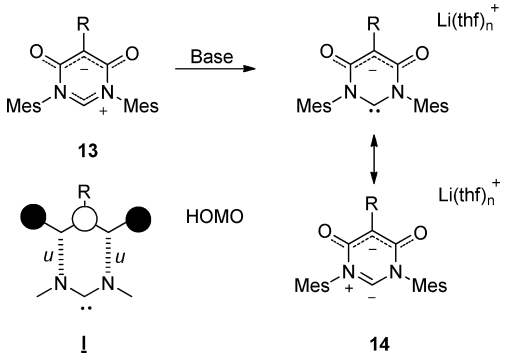


Thus, obviously NHCs have unknowingly been commercially available for more than 100 years.[25] The mesoionic compound imidazolium-4-aminide **9** and its isomer, the NHC **10**, show a similar behavior.[26] The mesoionic compound imidazolium-4-olate **11** has been converted into the anionic N-heterocyclic carbene **12**.[27] We believe that these very recent results are only the first examples of numerous betaine−carbene interconversions which await recognition and application.

A very small number of reports have dealt with conversions of cross-conjugated mesomeric betaines (CCMB) into N-heterocyclic carbenes. Thus, the CCMB **13** was recently transformed into the stable anionic N-heterocyclic carbene **14**[28] (Scheme 2). Characteristic of CCMB, in the canonical formulas the charges are strictly delocalized in separate parts of the molecule.[22] This translates into the MO theory in such a way that the N atoms of the cationic partial structure are joined to the anionic fragment of the molecule through nodal positions of the highest occupied molecular orbital (HOMO) **I**.[29,30] As a consequence, in the anionic NHC **14** a diaminocarbene fragment is bridged by union bonds ("*u*") through nodal, inactive positions of the HOMO of a 3-oxopropanolate anion.

The CCMBs pyrazolium-4-carboxylate **15** and imidazolium-4-carboxylate **16** are formal 1:1 adducts **II** and **IV** of heterocumulenes (such as CO_2) of the remote NHC pyrazol-4-ylidene and the abnormal NHC imidazol-4-ylidene, respectively[31] (Figure 2). Again, the anionic fragment of the betaines

Scheme 2. Architecture of a Negatively Charged N-Heterocyclic Carbene Derived from a Mesomeric Betaine



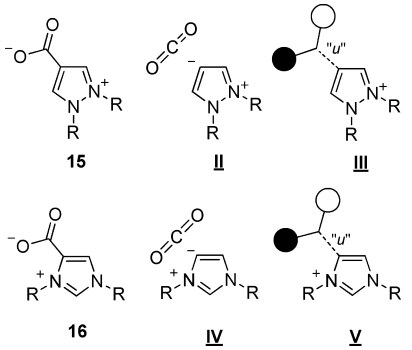


Figure 2. *Remote* (*r*NHC) and *abnormal* N-heterocyclic carbenes (*a*NHC) and their relationship to cross-conjugated mesomeric betaines (CCMB).

is joined through union bonds ("*u*") to the nodal position of the HOMO (cf. **III** and **V**). The generation of carbenes from these types of mesomeric betaines is seemingly limited due to harsh reaction conditions. The formation of pyrazol-4-ylidene by thermal decarboxylation of **15** was examined mass spectrometrically,[31] whereas imidazol-4-ylidene generated from **16** was trapped by isocyanates.[31]

In contrast, the thermal generation of N-heterocyclic carbenes from pseudo-cross-conjugated mesomeric betaines (PCCMB) proceeds under smooth conditions. PCCMBs have been defined on the basis of their characteristic dipole types[32] and their mesomeric structures, which include forms with an electron-sextet structure without internal octet stabilization.[22,30] Pyrazolium-3-carboxylates, -amidates, and -thioamidates **17** and their isomeric imidazoles **18** are precursors of N-heterocyclic carbenes which form thermally on extrusion of heterocumulenes such as CO_2, isocyanates, and thioisocyanates, respectively[33] (Figure 3, **VI** and **VII**). Vice versa, numerous examples of trapping reactions of NHC with heterocumulenes to give PCCMBs have been described.[34] Among these trapping reactions, adduct formations with boranes have been reported,[35] including those starting from PCCMBs.[36] A review on NHC−borane adducts appeared recently.[37] This reflects the remarkable development of the class of NHC−borane adducts which was considered rare, perhaps even exotic,[37] prior to 2008.

In continuation of our interest in mesomeric betaines,[38] organic polycations,[39] and N-heterocyclic carbenes[40] we describe here a series of imidazolium indolates which belong to the class of N-ylides related to conjugated mesomeric betaines (CMB). These are in equilibrium with their N-heterocyclic carbenes. The NHCs of imidazolium indolates, i.e.

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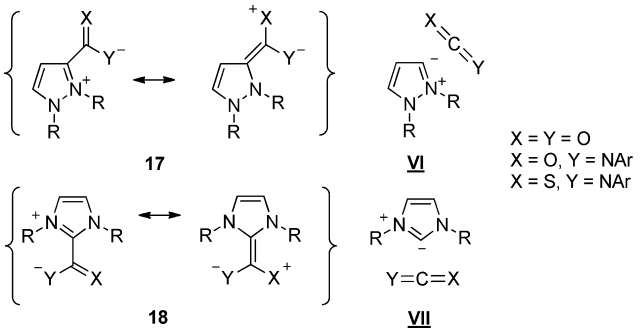


Figure 3. Heterocumulene adducts of N-heterocyclic carbenes forming a special class of mesomeric betaines, namely PCCMB.

1-(indol-2-yl)imidazol-2-ylidenes, undergo trapping reactions with sulfur. Triethylborane and triphenylborane proved to be suitable reagents to trap both forms, N-ylide as well as NHC, as the first representatives of a new boron-containing zwitterionic heterocyclic ring system. We present results of ^{1}H, ^{13}C, ^{7}Li, ^{15}N, and ^{11}B NMR spectroscopic examinations and a single-crystal X-ray structure analysis.

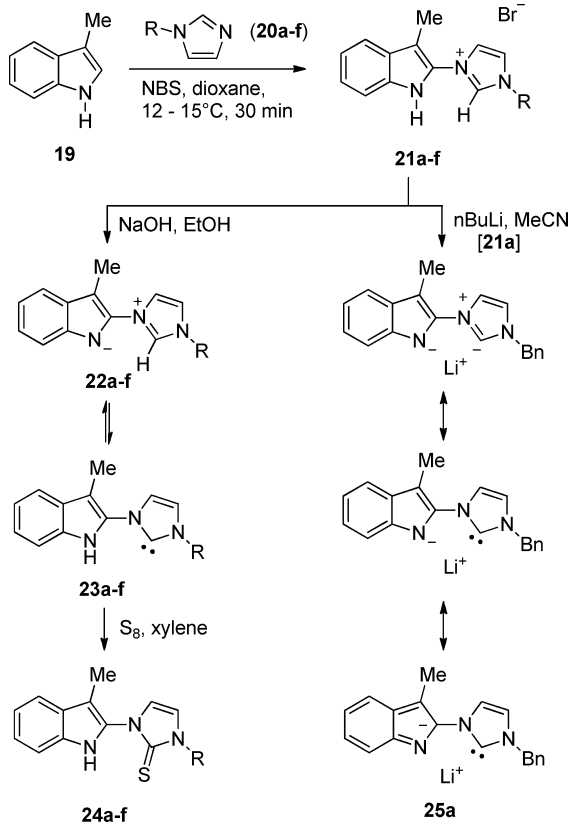
RESULTS AND DISCUSSION

The (indol-2-yl)imidazolium salts **21a–f** were prepared in good to quantitative yields on addition of NBS to a slightly cooled dioxane solution of 3-methylindole **19** and the imidazoles **20a–f**, respectively. After 30 min precipitates of the salts were filtered off (Scheme 3). Deprotonation of the salts **21a–f** to the mesomeric betaines **22a–f** was best accomplished by an ethanolic NaOH solution. The mesomeric betaines are stable, colorless to yellowish compounds and were obtained in high yields. On deprotonation, the NH resonance frequencies of **21a–f**, detectable between δ 12.04 and 12.16 ppm, disappear and the ^{15}N NMR signals are shifted considerably. Thus, the signals of **21a** at −251.8 (N_{indole}), −206.9 ($N1_{imidazolium}$) bearing the indolyl substituent, and −193.5 ppm ($N3_{imidazolium}$) adjacent to the benzyl group shift to −210.1 (N_{indole}), −196.2 ($N1_{imidazolium}$), and −195.0 ppm ($N3_{imidazolium}$) on conversion to **22a**.

The betaine **22a** was calculated to be ΔG = −9.3 kJ/mol more stable than the corresponding carbene **23a**. In DMSO-d_6 solution only the mesomeric betaines **22a–f** can be detected in the NMR spectra. Assuming an unimolecular mechanism, the betaine–carbene interconversion possesses a computed activation barrier of $\Delta G^{\ddagger}$ = 66.4 kJ/mol. The carbenes could be trapped by sulfur in boiling xylene, whereupon the thiones **24a–f** were formed in high to quantitative yields.

Treatment of **21a** with excess nBuLi in MeCN-d_3 led to the formation of lithium salts of the anionic N-heterocyclic carbene **25a**, three mesomeric structures of which are shown in Scheme 3. The sample was prepared at −40 °C under an inert atmosphere from freshly dried salt **21a** and proved to be stable under these conditions for a few hours. The carbene resonance frequency is detectable by NMR spectroscopy. Thus, the carbene atom of **25a** can be measured as an Li adduct at δ 181.4 ppm in the ^{13}C NMR spectra. The Li signal appears at δ 0.40 ppm in ^{7}Li NMR spectroscopy. In high-resolution electrospray ionization mass spectrometry, the anionic N-heterocyclic carbene **25a** is clearly detectable as a prominent peak in the anion detection mode (calcd 286.1344, found 286.1337). A DFT calculation predicts an anionic N-heterocyclic carbene possessing a bridging Li cation as the most stable form (cf. the Supporting Information).

Scheme 3. Trapping of N-Heterocyclic Carbenes 23a–f, Which Are in Equilibrium with N-Ylides 22a–f, and Formation of the Anionic N-Heterocyclic Carbene 25a



	21	22/23	24
a: R =-CH_2-phenyl	76 %	50%	96%
b: R = -CH_2-(2-Cl-phenyl)	72 %	79%	95%
c: R = -CH_2-(3-Me-phenyl)	78 %	70%	90%
d: R = -CH_2-(2-naphthyl)	67 %	94%	94%
e: R = -$CHPh_2$	72 %	79%	62%
f: R = -4-dimethylaminophenyl	100 %	76%	54%

The betaines **22a–f** are members of the class of N-ylides which are closely related to conjugated heterocyclic mesomeric betaines (CMB) (Figure 4). Characteristic canonical formulas such as **B** can be drawn, and common atoms for either charge can be dissected from mesomeric structures such as **A** and **C**. It should be noted here that the negative charge is delocalized in

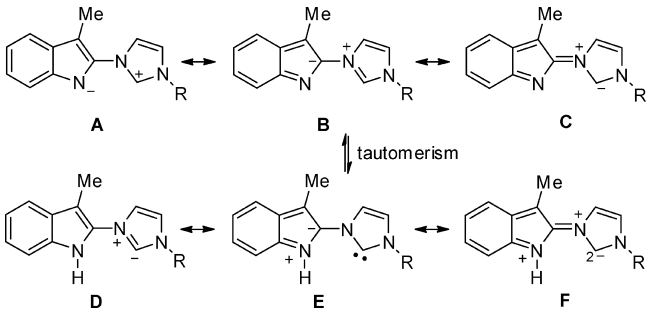


Figure 4. Mesomeric structures of the target N-ylides **22** (**A–C**) and their tautomeric carbenes **23** (**D–F**).

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the π-electron system according to the definition of mesomeric betaines, and a negative charge can be drawn on the potential carbene center C2 of the imidazolium ring (**C**). Canonical structures of the tautomeric carbene includes the usual zwitterionic representation **D**, the electron sextet structure **E**, and a tetrapolar structure **F** with two negative charges located on C2 of the imidazole.

As the distinct classes of mesomeric betaines differ in their frontier orbital profiles (see above), we were interested in calculating changes of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) on betaine–carbene conversion. The frontier orbital profile is shown in Figure 5. The bond between $N1_{imidazolium}$ and $C2_{indolate}$ was

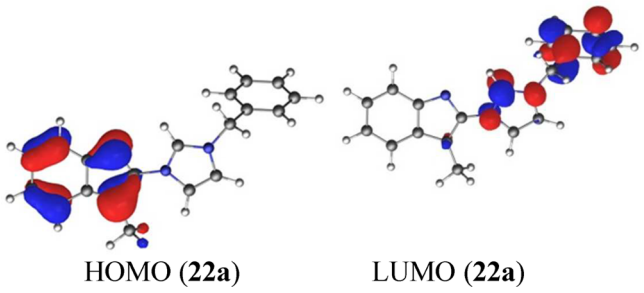


Figure 5. Frontier orbital profile of **22a**.

calculated to have a bond length of 142.1 pm (**22a**), which corresponds to a 33% double-bond character according to the Pauling–Brockway equation. The same DFT calculation predicts a torsion angle of 4.6° between the two partial structures in vacuo.

On conversion into the carbene form, the π-type HOMO changes only slightly according to the calculations (Figure 6).

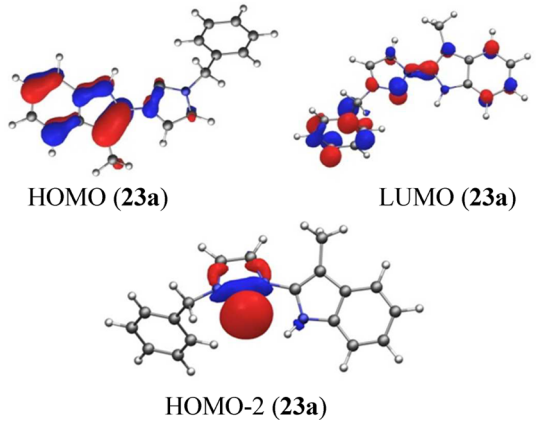
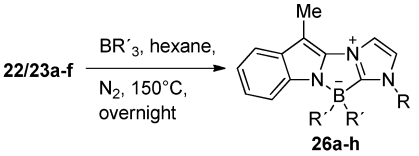


Figure 6. Frontier orbital profile and the σ-type HOMO-2 of **23a**.

The HOMO-2 is mainly a σ-type molecular orbital. On conversion from the ylide into the carbene form, the permanent dipole moment decreases dramatically. Thus, ylide **22a** has a calculated dipole moment of 11.99 D, which changes to 3.67 D on carbene formation.

We the found that BEt_3 and BPh_3 are suitable trapping reagents for both forms, N-ylide and N-heterocyclic carbene, as treatment of suspensions of the betaines **22a–f** with triethylborane in hexane under an inert atmosphere at 150 °C in a sealed tube resulted in the formation of the imidazodiazaboroloindoles **26a–f** as colorless, slightly fluorescent crystals (Scheme 4). These compounds are the first examples of a new heterocyclic ring system. On reaction of **22a**

Scheme 4. Borane Adduct Formation Starting from the N-Ylide–NHC Equilibrium



	R	R´	yield
a	-CH_2-phenyl	Et	67%
b	-CH_2-(2-Cl-phenyl)	Et	65%
c	-CH_2-(3-Me-phenyl)	Et	31%
d	-CH_2-(2-naphthyl)	Et	67%
e	-$CHPh_2$	Et	84%
f	-4-dimethylaminophenyl	Et	78%
g	-CH_2-phenyl	Ph	42%
h	-CH_2-phenyl	C_6F_5	0%

with triphenylborane, **26g** was formed. Perfluorophenylborane failed to undergo the reaction to **26h** under the conditions applied.

The structure of these compounds in solution was elucidated by detailed NMR investigations, including ^{1}H, ^{13}C, and ^{1}H,^{15}N-HMBC measurements (cf. the Supporting Information). The boron atoms give singlets between δ −1.6 and 0.0 ppm in ^{11}B NMR spectroscopy. Related structures are extremely rare. 4,4,8,8-Tetraethyl-1,5-dimethylimidazabole,[41] *B,B,B′,B′*-tetraethylthiazabole,[42] and its triazabole derivative[43] also possess $N–B(Et)_2–C_{carbene}$ structure elements which we compared to our molecules; their ^{11}B NMR resonance frequencies are at δ −6.3 ($^1J_{CB}$ = 54 Hz), −2.5 , and −6.1 ppm (s), respectively. As the ring system is not planar, the diastereotopic ethyl groups split into two sets of signals. Despite the often observed quadrupole broadening and spin–spin coupling to the neighboring boron atom in NHC–borane adducts which prevent the detection of the carbene carbon atoms, the C2 atom of the imidazole moiety gives a resonance frequency at δ 175.8 ppm (**26a**) in the ^{13}C NMR spectrum taken in $CDCl_3$. This chemical shift proves the formation of a single bond between the boron atom and the C2 carbon, which was additionally detected by an HMBC cross-peak originating from a $^3J_{C,H}$ coupling of the C2 carbon with the methylene protons of the alkyl borate. The corresponding signals of the aforementioned imidazabole and thiazabole are δ 164 (br, C_6d_6) and 195 ppm (br, C_6d_6), respectively. The N atoms of **26a** give resonance frequencies at δ −218.7 (N_{indole}), −182.3 ($N1_{imidazolium}$), and −199.8 ppm ($N3_{imidazolium}$). The last atom mentioned, benzyl-substituted nitrogen, was identified by its ^{1}H,^{15}N-HMBC signal with the benzylic protons, whereas the indole nitrogen was assigned on the basis of a coupling with the ortho proton of the annelated phenyl ring and, additionally, by means of a cross-peak with the BCH_2 protons. Thus, the combination of both cross-peaks from these methylene protons proves the formation of the central diazaborolium-type five-membered ring in **26a**. The benzylic protons of **26a** cannot be removed either by Proton Sponge in $CDCl_3$ or by NaOD in THD-d_8, as evidenced by ^{1}H NMR spectroscopy, so that an imidazolium ylide partial structure in equilibrium can be excluded from consideration.

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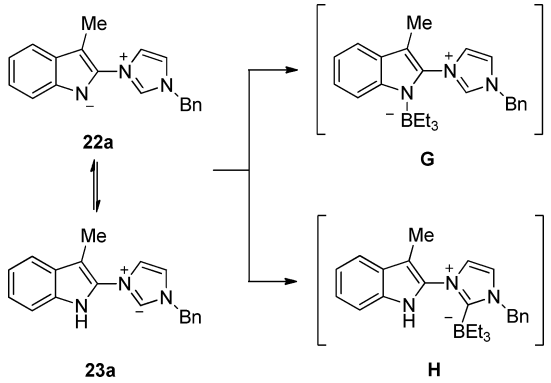
Single crystals of **26a**, obtained from *p*-xylene/hexane, were subjected to an X-ray analysis. The compound crystallized in the monoclinic system. The crystallographically determined B–$C_{carbene}$ bond is longer (165.2(2) pm) than the B–C_{ethyl} bonds (162.3(2)/161.5(2) pm). The boron–nitrogen bond was measured to be 158.7(2) pm. Thus, in **26a** the B–$C_{carbene}$ bond is slightly longer than the B–C bonds in structures with sterically hindered groups. As example, the corresponding bond in the IDipp/$B(C_6F_5)_3$ adduct was found to be 166.3(5) pm,[43] and those in adducts of 2,3,4,5-tetramethyl-1,3-imidazol-2-ylidene/$B(C_6F_5)_3$ were found to be 164.07(18)[44] and 159.2(2) pm.[45] The angle N–$C_{carbene}$–N was determined to be 105.54(11)°, and this value characteristically is between the angles of free carbenes (101°) and imidazolium salts (108°).[37] The torsion angle between the imidazolium moiety and the indole ring was determined to be −4.0(2)°.

The frontier orbital profile of **26a** is presented in the Supporting Information. As expected, the HOMO and LUMO are π orbitals.

To gain insight into the mechanism, we monitored the reaction of ylide **22a** with BEt_3 by NMR spectroscopy in MeCN-d_3 at room temperature. Surprisingly, no adduct formation between N_{indole} and BEt_3 was detectable under these conditions, although a DFT calculation predicted that the initial coordination of triethylborane to the indolate nitrogen of **22a** to **G** is energetically slightly more favored by 19.7 kJ/mol than the coordination to the carbene carbon atom of **23a** to **H** (Scheme 5). Instead, a $^1H,^{15}N$-HMBC spectrum of a mixture of

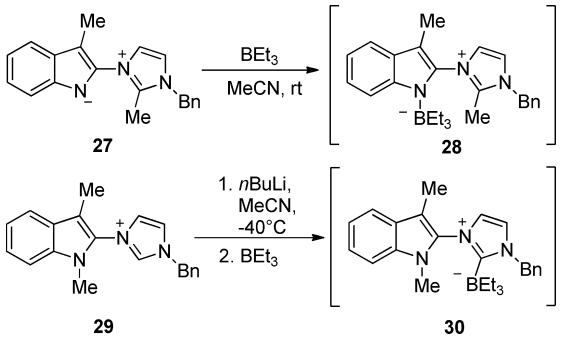
Scheme 5. Initial Borane Adduct Formation According to NMR Investigations



22a and BEt_3 clearly showed a signal at δ −250.2 ppm, which is characteristic of an NH group. Fortunately, this 2D hetero correlation spectrum additionally showed a one-bond coupling N–H cross-peak of this indole nitrogen with the slightly broadened proton singlet at approximately 9.35 ppm. Thus, the former N-ylide nitrogen is reprotonated, whereas the trialkylborane attacks the imidazolium carbene atom to give the corresponding NHC–-borane adduct **H**. The formation of the B–$C_{carbene}$ bond is confirmed by a ^{11}B shift of −12.7 ppm. The $N1_{imidazolium}$ and $N3_{imidazolium}$ signals of **H** were unambiguously assigned to resonance frequencies at δ −194.3 and −202.8 ppm in the ^{15}N NMR spectra.

To prove these results, we prepared the methylated derivatives **27** and **29** as model compounds (Scheme 6). On addition of triethylborane to **27** in MeCN-d_3 at room temperature, we were not able to observe any shift changes in the ^1H NMR spectra, in accordance with the results

Scheme 6. Model Compounds



described above. Deprotonation of **29**, however, with nBuLi in cyclohexane in MeCN-d_3 at −40 °C resulted in the formation of the free carbene and its Li adduct. The carbene can unambiguously be detected by a carbon NMR signal at δ 201.8 ppm, whereas the Li adduct shows a characteristic resonance frequency at δ 184.2 ppm. Then, excess BEt_3 in MeCN-d_3 was added to the mixture and the borane formation was monitored by NMR spectrometry. The formation of new signals was observed while the original signals disappeared over a period of 24 h at room temperature. Attempts to isolate **30**, however, failed due to decomposition of the material during the workup procedure.

CONCLUSIONS

The chemistry of mesomeric betaines and the chemistry of N-heterocyclic carbenes have an area of overlap which has not yet been examined in detail. In this report, examples of N-ylides, which form a class of mesomeric betaines of its own, are in equilibrium with N-heterocyclic carbenes. Thus, the equilibrium of the N-ylides 2-(imidazolium-3-yl)-3-methylindolates and their tautomeric N-heterocyclic carbenes (3-methylindol-2-yl)imidazol-2-ylidenes (NHC) can be shifted by trapping of the carbene by sulfur with formation of imidazolethiones. Triethylborane and triphenylborane proved to be suitable reagents to trap either form with formation of a new ring system. Thus, we describe the first representatives of new zwitterionic borane adducts, imidazo[2′,1′:3,4][1,4,2]-diazaborolo[1,5-*a*]indolium-11-ides. In these compounds, the boron atom bridges the carbene center with the former negatively charged ylide N atom. DFT calculations reveal that HOMO and LUMO of the N-ylide as well as of the N-heterocyclic carbene are π-type orbitals; the HOMO-2 of the carbene was found to be a σ-type orbital. Characteristic ^{11}B and ^{15}N NMR resonance frequencies were identified, which allowed an NMR monitoring of the reaction.

We believe that a closer inspection of the characteristic features of mesomeric betaines is a stimulus for the development of the ever-growing chemistry of N-heterocyclic carbenes and their relatives.

EXPERIMENTAL SECTION

General Remarks. The ^1H, ^{13}C, ^{15}N, and ^{11}B NMR spectra were recorded in DMSO-d_6, $CDCl_3$, or CD_3CN at 400 MHz (^1H NMR) and 600 MHz (^1H NMR), respectively. The chemical shifts are reported in ppm relative to internal standard tetramethylsilane (δ 0.00 ppm), nitromethane, and boron trifluoride etherate, respectively. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad. Peak assignments were accomplished by results of HMBC-

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NMR, HSQC-NMR, and HH-NOESY measurements. FT-IR spectra were obtained in the range 400−4000 cm^{-1} (2.5% pellets in KBr). Samples for ESI mass spectrometry were sprayed from methanol at 0 V fragmentor voltage unless otherwise noted. The melting points were measured by differential scanning calorimetry and are not corrected. Yields are not optimized. All density functional theory (DFT) calculations were carried out by using the Jaguar 7.7.107 software running on Linux 2.6.18−238.el5 SMP (x86_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI 1.3.4. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay−Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima or first-order saddle points by the absence of imaginary frequencies or occurrence of one imaginary frequency, respectively. Plots were obtained using Maestro 9.1.207, the graphical interface of Jaguar. Thermodynamic corrections were estimated from unscaled frequencies, using standard formulas in the ideal gas harmonic oscillator approximation as implemented in Jaguar, and refer to a standard state of 298.15 K and 1 mol/dm^3 concentration. Charges were obtained using the natural atomic orbital and natural bond orbital analysis which is included in Jaguar NBO 5.0.[46] Calculations of the reactions in the solution phase (toluene) displayed essentially no energy differences (<2 kJ/mol), in comparison to the calculations performed for reactions in the gas phase.

General Procedure for the Synthesis of the Salts 21a−f. A solution of 3-methylindole (145 mg, 1.0 mmol) and the corresponding imidazoles (1.3 mmol) in 3 mL of dioxane was stirred at 12−15 °C while NBS (179 mg, 1.0 mmol) was added over a period of 5 min. After stirring for an additional 30 min the precipitates were filtered off, washed with a small amount of dioxane, and dried in vacuo.

*1-Benzyl-3-(3-methyl-1H-indol-2-yl)imidazolium Bromide (**21a**).* 1-Benzylimidazole (211 mg, 1.3 mmol) was used. Recrystallization from i-PrOH/H_2O gave colorless crystals, yield 280 mg (76%), mp >300 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.32 (s, 3 H, Me), 5.71 (s, 2 H, CH_2), 7.15 (ddd, 1 H, J = 8.0 Hz, J = 7.0 Hz, J = 0.8 Hz), 7.27 (ddd, 1 H, J = 8.2 Hz, J = 7.0 Hz, J = 1.0 Hz), 7.40−7.48 (m, 4 H), 7.63−7.66 (m, 3 H), 8.25 (dd, 1 H, $J_1 \approx J_2$ = 1.8 Hz), 8.26 (dd, 1 H, $J_1 \approx J_2$ = 1.8 Hz), 10.23 (m, 1 H), 12.16 (br s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 8.2, 52.7, 104.6, 112.2, 119.9, 120.5, 123.5, 124.0, 124.3, 125.5, 127.4, 129.1, 129.4, 129.5, 133.9, 135.1, 137.5 ppm. ^{15}N NMR (DMSO-d_6, 61 MHz): δ −251.8, −206.9, −193.5 ppm. ESI-MS: m/z (%) 288.1 (100) [M^+]. IR (KBr): ν 3062, 1737, 1632, 1566, 1543, 1495, 1454, 1330, 1228, 1170, 1124, 1101, 1079, 888, 740, 709, 646, 626, 563, 464 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{18}N_3^+$ 288.1501, found 288.1500.

*1-(2-Chlorobenzyl)-3-(3-methyl-1H-indol-2-yl)imidazolium Bromide (**21b**).* 2-Chlorobenzylimidazole (256 mg; 1.3 mmol) was used. The salt **21b** was isolated as colorless crystals, mp 210 °C, yield 289 mg (72%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.29 (s, 3 H, Me), 5.72 (s, 2 H, CH_2), 7.16 (dd, 1 H, $J_1 \approx J_2$ = 7.6 Hz), 7.28 (dd, 1 H, $J_1 \approx J_2$ = 7.6 Hz), 7.45−7.67 (m, 6 H), 8.09 (s, 1 H), 8.25 (s, 1 H), 9.94 (s, 1 H), 12.04 (s, 1 H, NH) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.6, 50.5, 104.4, 111.7, 119.5, 120.0, 123.3, 123.6, 124.0, 124.9, 126.8, 128.0, 129.9, 131.0, 131.0, 131.6, 132.9, 133.4, 137.8 ppm. ESI-MS: m/z (%) 322.0 (100) [M^+]. IR (KBr): ν 2923, 1629, 1562, 1439, 1329, 1123, 1079, 1050, 776, 739, 681, 646, 624, 563, 444, 411 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{17}ClN_3^+$ 322.1106, found 322.1111.

*3-(3-Methyl-1H-indol-2-yl)-1-(3-methylbenzyl)imidazolium Bromide (**21c**).* 3-Methylbenzylimidazole (229 mg, 1.3 mmol) was used. Salt **21c** was isolated as colorless crystals, mp 236 °C, yield 298 mg (78%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.31 (s, 3 H, Me), 2.34 (s, 3 H, Me), 5.57 (s, 2 H, CH_2), 7.14−7.18 (m, 1 H), 7.23−7.30 (m, 2 H), 7.35−7.36 (m, 2 H), 7.39 (s, 1 H), 7.46 (d, 1 H, J = 8.2 Hz), 7.65 (d, 1 H, J = 8.0 Hz), 8.16 (dd, 1 H, $J_1 \approx J_2$ = 1.7 Hz), 8.21 (dd, 1 H, $J_1 \approx J_2$ = 1.7 Hz), 8.21 (s, 1 H), 12.04 (s, 1 H, NH) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.6, 20.9, 52.3, 104.2, 111.7, 119.5, 120.0, 123.0, 123.5, 123.9, 125.0, 125.6, 126.8, 128.9, 129.1, 129.5, 133.4, 134.4, 137.1, 138.3 ppm. ESI-MS: m/z (%) 302.2 (100) [M^+]. IR (KBr): ν 2961, 1568, 1446, 1332, 1238, 1118, 1084, 867, 744, 727, 626, 562, 445, 437 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{20}N_3^+$ 302.1657, found 302.1654.

*3-(3-Methyl-1H-indol-2-yl)-1-(naphthalen-2-ylmethyl)-imidazolium Bromide (**21d**).* 1-(Naphthalen-2-ylmethyl)imidazole (277 mg) was used. Salt **21d** was isolated as colorless crystals, mp 262 °C, yield 381 mg (91%). ^{1}H NMR (DMSO-d_6, 400 MHz): 2.32 (s, 3 H, Me), 5.80 (s, 2 H, CH_2), 7.16 (ddd, 1 H, J = 8.0 Hz, J = 7.0 Hz, J = 0.8 Hz), 7.28 (ddd, 1 H, J = 8.2 Hz, J = 7.0 Hz, J = 1.1 Hz), 7.46 (d, 1 H, J = 8.2 Hz), 7.58−7.61 (m, 2 H), 7.66 (d, 1 H, J = 8.0 Hz), 7.69 (dd, 1 H, J = 8.6 Hz, J = 1.7 Hz), 7.96−7.99 (m, 2 H), 8.03 (d, 1 H, J = 8.6 Hz), 8.12 (s, 1 H), 8.22−8.24 (m, 2 H), 10.06 (dd, 1 H, $J_1 \approx J_2$ = 1.6 Hz), 12.05 ppm (s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.7, 52.6, 104.2, 111.7, 119.5, 120.0, 123.1, 123.5, 123.9, 125.1, 125.8, 126.8, 126.8, 126.9, 127.7, 127.8, 127.9, 128.8, 131.9, 132.7, 132.8, 133.4, 137.3 ppm. ESI-MS: m/z (%) 338.1 (100) [M^+]. IR (KBr): ν 3053, 1632, 1566, 1544, 1454, 1329, 1122, 1079, 856, 819, 775, 739, 689, 646, 623, 611, 263, 472, 409 cm^{-1}. HR-ESI-MS: calcd for $C_{23}H_{20}N_3^+$ 338.1657, found 338.1656.

*1-Benzhydryl-3-(3-methyl-1H-indol-2-yl)-1H-imidazolium Bromide (**21e**).* A 256 mg portion of 1-benzhydrylimidazole was used. Salt **21e** was isolated as white crystals, mp 188 °C, yield 320 mg (72%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.29 (s, 3 H, Me), 3.37 (s, 2 H, CH_2), 7.15 (ddd, 1 H, J = 7.8 Hz, J = 7.0 Hz, J = 0.8 Hz), 7.27 (ddd, 1 H, J = 8.2 Hz, J = 7.0 Hz, J = 1.0 Hz), 7.41−7.54 (m, 12 H), 7.65 (d, 1 H, J = 7.8 Hz), 8.16 (dd, 1 H, $J_1 \approx J_2$ = 1.8 Hz), 8.33 (dd, 1 H, $J_1 \approx J_2$ = 1.8 Hz), 9.87 (s, 1 H), 12.04 ppm (s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.7, 66.2, 104.3, 111.7, 119.4, 120.0, 122.7, 123.6, 124.4, 125.0, 126.8, 128.3, 129.0, 129.2, 133.4, 136.8, 137.3 ppm. ESI-MS: m/z (%) 364.0 (100) [M − 80]. IR (KBr): ν 3016, 1739, 1632, 1555, 1494, 1446, 1336, 1218, 1121, 1076, 743, 714, 696, 655, 593, 572, 410 cm^{-1}. HR-ESI-MS: calcd for $C_{25}H_{22}N_3^+$ 364.1814, found 364.1806.

*1-(4-(Dimethylamino)phenyl)-3-(3-methyl-1H-indol-2-yl)-1H-imidazolium Bromide (**21f**).* A sample of 249 mg of 1-(4-dimethylamino)phenylimidazole was used. Salt **21f** was isolated as white crystals, mp 262 °C, yield 397 mg (100%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.37 (s, 3 H, 3-Me), 3.01 (s, 6 H, NMe_2), 6.94 (d, 2 H, H-*o*-PhNMe_2, J = 9.2 Hz), 7.17 (ddd, 1 H, H-5, J = 7.9 Hz, J = 7.0 Hz, J = 0.8 Hz), 7.30 (ddd, 1 H, H-6, J = 8.2 Hz, J = 7.0 Hz, J = 1.1 Hz), 7.49 (d, 1 H, H-7, J = 8.2 Hz), 7.67 (d, 1 H, H-4, J = 7.9 Hz), 7.73 (d, 2 H, H-*m*-PhNMe_2, J = 9.2 Hz), 8.40 (dd, 1 H, $H_{imidazole}$, $J \approx J_4$ = 1.8 Hz), 8.55 (dd, 1 H, $H_{imidazole}$, $J \approx J_4$ = 1.8 Hz), 10.20 (dd, 1 H, $H_{imidazole}$, J_4 = 1.6 Hz), 12.07 ppm (br s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.7, 40.0, 104.4, 111.7, 112.3, 119.5, 120.0, 121.8, 122.9, 123.3, 123.6, 124.0, 125.1, 126.9, 133.4, 134.9, 151.0 ppm. ESI-MS: m/z (%) 317.1 (100) [M − 80]. IR (KBr): ν 3059, 1608, 1527, 1441, 1373, 1325, 1192, 1116, 1066, 815, 781, 754, 666, 631, 607, 510, 444 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{21}N_4^+$ 317.1766, found 317.1765.

General Procedure for the Formation of Ylides 22a−f. The corresponding salt (1.0 mmol) was dissolved in 10 mL of aqueous EtOH (50%). Then, 1.5 equiv of a 3 M solution of NaOH was added. The resulting precipitate was filtered off, washed two times with water, and dried in vacuo.

*2-(1-Benzyl-1H-imidazolium-3-yl)-3-methylindolate (**22a**).* A sample of the salt **21a** (367 mg, 1.0 mmol) was used. The ylide **22a** was obtained as white crystals, mp 106 °C, yield 178 mg (62%). ^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.37 (s, 3 H, Me), 5.47 (s, 2 H, CH_2), 6.72 (ddd, 1 H, J = 7.9 Hz, J = 6.8 Hz, J = 1.1 Hz), 6.78 (ddd, 1 H, J = 8.0 Hz, J = 6.8 Hz, J = 1.4 Hz), 7.26 (d, 1 H, J = 8.0 Hz), 7.33 (d, 1 H, J = 7.9 Hz), 7.38−7.51 (m, 5 H, Ph), 7.86 (s, 1 H), 8.08 (s, 1 H), 9.73 (s, 1 H) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 9.7, 52.4, 93.8, 115.4, 116.9, 117.6, 117.8, 122.2, 122.4, 128.7, 129.2, 129.5, 131.2, 134.1, 135.7, 137.0, 143.0 ppm. ^{15}N NMR (DMSO-d_6, 61 MHz): δ −195.0, −196.2, −210.1 ppm. ESI-MS: m/z (%) 288.1 (100) [M − 80]. IR (KBr): ν 1633, 1566, 1543, 1496, 1454, 1383, 1333, 1231, 1170, 1124, 1102, 1079, 1006, 888, 821, 778, 757, 709, 647, 629, 564, 464, 407 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{18}N_3^+$ 288.1501, found 288.1501.

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*2-(1-(2-Chlorobenzyl)-1H-imidazolium-3-yl)-3-methylindolate (**22b**).* A sample of 401 mg of **21b** was used. The ylide **22b** was isolated as a yellowish powder, mp 95 °C, yield 254 mg (79%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.36 (s, 3 H, Me), 5.64 (s, 2 H, CH_2), 6.66 (dd, 1 H, J = 7.4 Hz, J = 7.0 Hz), 6.72 (dd, 1 H, J = 7.9 Hz, J = 7.0 Hz), 7.21 (d, 1 H, J = 8.0 Hz), 7.28 (d, 1 H, J = 7.6 Hz), 7.42−7.50 (m, 3 H), 7.58−7.61 (m, 1 H), 7.81 (s, 1 H), 8.12 (s, 1 H), 9.63 ppm (s, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 9.3, 49.9, 92.9, 114.7, 116.5, 116.9, 117.0, 121.7, 122.1, 127.7, 128.0, 129.5, 129.8, 130.4, 130.7, 130.8, 132.5, 132.6, 134.0, 136.8, 142.8 ppm. ESI-MS: m/z (%) 322.1 (100) [M + 1]. IR (KBr): ν 1546, 1442, 1321, 1161, 1113, 1055, 821, 737, 680, 625, 452 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{17}ClN_3^+$ 322.1111, found 322.1106.

*3-Methyl-2-(1-(3-methylbenzyl)-1H-imidazolium-3-yl)indolate (**22c**).* A sample of 381 mg of **21c** was used. The ylide **22c** was isolated as a yellowish powder, mp 93 °C, yield 211 mg (70%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.33 (s, 3 H, Me), 2.36 (s, 3 H, Me), 5.44 (s, 2 H, CH_2), 6.66−6.76 (m, 2 H), 7.21−7.23 (m, 2 H), 7.28−7.35 (m, 4 H), 7.88 (s, 1 H), 8.08 (s, 1 H), 9.70 (s, 1 H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 9.3, 20.9, 51.9, 92.8, 114.7, 116.4, 116.9, 117.0, 121.6, 121.9, 125.3, 128.8, 128.9, 129.3, 130.8, 133.4, 135.1, 136.8, 138.3, 142.7 ppm. ESI-MS: m/z (%) 302.1 (100) [M + 1]. IR (KBr): ν 1442, 1321, 1161, 1113, 1055, 821, 737, 680, 625, 452 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{20}N_3^+$ 302.1657, found 302.1654.

*3-Methyl-2-(1-(naphthalen-2-ylmethyl)-1H-imidazolium-3-yl)-indolate (**22d**).* A sample of 417 mg of **21d** was used. The ylide **22d** was isolated as a yellowish powder, mp 212 °C, yield 317 mg (94%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.38 (s, 3 H, Me), 5.66 (s, 2 H, CH_2), 6.67 (ddd, 1 H, J = 7.6 Hz, J = 6.7 Hz, J = 1.0 Hz), 6.74 (ddd, 1 H, J = 7.9 Hz, J = 6.7 Hz, J = 1.3 Hz), 7.23 (d, 1 H, J = 7.9 Hz), 7.29 (s, 1 H, J = 7.6 Hz), 7.54−7.59 (m, 2 H), 7.63 (dd, 1 H, J = 8.5 Hz, J = 1.7 Hz), 7.92−7.96 (m, 3 H), 7.99 (d, 1 H, J = 8.5 Hz), 8.03 (s, 1 H), 8.10 (s, 1 H), 9.77 ppm (s, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 9.4, 52.0, 92.7, 114.6, 116.6, 116.9 (2 C), 121.6, 122.0, 125.6, 126.7 (2 C), 127.4, 127.7, 127.9, 128.8, 130.9, 132.7, 132.7, 133.5, 137.1, 142.9 ppm. ESI-MS: m/z (%) 338.1 (100) [M − 80]. IR (KBr): ν 1549, 1443, 1318, 1292, 1161, 1115, 863, 821, 777, 737, 614, 476 cm^{-1}. HR-ESI-MS: calcd for $C_{23}H_{20}N_3^+$ 338.1657, found 338.1656.

*2-(1-Benzhydryl-1H-imidazolium-3-yl)-3-methylindolate (**22e**).* A sample of 401 mg of **21e** was used. The ylide **22e** was isolated as a yellowish powder, mp 229 °C, yield 287 mg (79%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.36 (s, 3 H, Me), 5.64 (s, 2 H, CH_2), 6.66 (dd, 1 H, J = 7.4 Hz, J = 7.0 Hz), 6.72 (dd, 1 H, J = 7.9 Hz, J = 7.0 Hz), 7.21 (d, 1 H, J = 8.0 Hz), 7.28 (d, 1 H, J = 7.6 Hz), 7.42−7.50 (m, 3 H), 7.58−7.61(m, 1 H), 7.81 (s, 1 H), 8.12 (s, 1 H), 9.63 ppm (s, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 9.3, 49.9, 92.9, 114.7, 116.5, 116.9, 117.0, 121.7, 122.1, 127.7, 128.0, 129.5, 129.8, 130.4, 130.7, 130.8, 132.5, 132.6, 134.0, 136.8, 142.8 ppm. ESI-MS: m/z (%) 322.1 (100) [M + 1]. IR (KBr): ν 1536, 1392, 1324, 1291, 1239, 1152, 1111, 1073, 834, 752, 729, 701, 656, 641, 475, 411 cm^{-1}. HR-ESI-MS: calcd for $C_{25}H_{22}N_3^+$ 364.1814, found 364.1806.

*2-(1-(4-(Dimethylamino)phenyl)-1H-imidazolium-3-yl)-3-methyl-indolate (**22f**).* A sample of 397 mg of **21f** was used. The ylide **22f** was isolated as a yellowish powder, mp 110 °C, yield 240 mg (76%). ^{1}H NMR (DMSO-d_6, 400 MHz): 2.42 (s, 3 H, Me), 2.99 (s, 6 H, NMe_2), 6.69 (dd, 1 H, J = 7.4 Hz, J = 7.4 Hz), 6.76 (dd, 1 H, J = 7.6 Hz, J = 7.4 Hz), 6.88 (d, 2 H, 9.0 Hz), 7.26 (d, 1 H, J = 7.6 Hz), 7.32 (d, 1 H, J = 7.4 Hz), 7.70 (d, 2 H, 9.0 Hz), 8.24 (s, 1 H), 8.28 (s, 1 H), 9.86 ppm (s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 9.2, 93.6, 112.3, 112.7, 114.8, 116.5, 117.0, 117.1, 120.4, 120.9, 122.2, 122.6, 122.8, 123.9, 125.5, 130.8, 131.3, 136.7, 142.6, 150.7 ppm. ESI-MS: m/z (%) 317.1 (25) [M + 1]. IR (KBr): ν 1606, 1519, 1442, 1332, 1298, 1236, 1092, 1055, 944, 810, 741, 625, 517 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{21}N_4^+$ 317.1766, found 317.1765.

General Procedure for the Formation of Thiones 24a−f. A flask was charged with the ylide (0.5 mmol), sulfur (32 mg, 1.0 mmol), and *p*-xylene (5 mL), and the mixture was stirred and boiled for 3 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether).

*1-Benzyl-3-(3-methyl-1H-indol-2-yl)-1H-imidazole-2(3H)-thione (**24a**).* A sample of the betaine **22a** (144 mg, 0.5 mmol) was used. The thione **24a** was isolated in 96% yield (153 mg), mp 154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.31 (s, 3 H, Me), 5.31 (s, 2 H, CH_2), 6.69 (d, 1 H, $H_{imidazole}$, J = 2.5 Hz), 6.92 (d, 1 H, $H_{imidazole}$, J = 2.5 Hz), 7.15 (ddd, 1 H, 5-H, J = 7.9 Hz, J = 7.0 Hz, J = 1.0 Hz), 7.24 (ddd, 1H, 6-H, J = 8.2 Hz, J = 7.0 Hz, J = 1.2 Hz), 7.35−7.40 (m, 6 H, Ar), 7.56 (d, 1 H, H-4, J = 7.9 Hz), 9.56 (br s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ 8.8, 51.3, 104.6, 111.5, 117.3, 118.3, 119.0, 119.9, 123.1, 127.7, 128.4, 128.4, 128.5, 129.0, 133.7, 135.2, 163.5 ppm. ESI-MS: m/z (%) 320.0 (100) [M + 1]. IR (KBr): ν 3356, 3091, 2918, 1629, 1494, 1471, 1399, 1325, 1299, 1241, 745, 714, 670, 470, 433 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{18}N_3S^+$ 320.1221, found 320.1217.

*1-(2-Chlorobenzyl)-3-(3-methyl-1H-indol-2-yl)-1H-imidazole-2(3H)-thione (**24b**).* A sample of 161 mg of **22b** was used. Thione **24b** was isolated in 95% yield (168 mg), mp 142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.31 (s, 3 H, Me), 5.44 (s, 2 H, CH_2), 6.79 (d, 1 H, J = 2.5 Hz), 6.94 (d, 1 H, J = 2.5 Hz), 7.13−7.17 (m, 1 H), 7.22−7.33 (m, 3 H), 7.36 (d, 1 H, J = 8.1 Hz), 7.43−7.47 (m, 2 H), 7.56 (d, 1 H, J = 7.9 Hz), 9.55 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.8, 48.7, 104.8, 111.5, 117.6, 118.4, 119.1, 120.0, 123.2, 127.5, 127.8, 128.4, 129.9, 129.9, 130.8, 133.0, 133.8, 133.8, 163.9 ppm. GC-MS: m/z (%) 353.0 (25) [M$^+$]. IR (KBr): ν 3159, 1628, 1469, 1399, 1311, 1237, 1054, 744, 135, 705, 673, 588, 239, 451, 426 cm^{-1}. HR-ESI-MS: calcd for $C_{19}H_{16}N_3NaSCl^+$ 376.0651, found 376.0651.

*1-(3-Methyl-1H-indol-2-yl)-3-(3-methylbenzyl)-1H-imidazole-2(3H)-thione (**24c**).* A sample of 151 mg of **22c** was used. Thione **24c** was isolated in 90% yield (150 mg), mp 156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.31 (s, 3 H, Me), 2.37 (s, 3 H, Me), 5.26 (s, 2 H, CH_2), 6.68 (d, 1 H, J = 2.5 Hz), 6.92 (d, 1 H, J = 2.5 Hz), 7.13−7.30 (m, 6 H), 7.37 (d, 1 H, J = 8.2 Hz), 7.56 (d, 1 H, J = 7.9 Hz), 9.59 (br.s., 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.8, 21.5, 51.4, 104.7, 111.5, 117.4, 118.3, 119.1, 120.0, 123.2, 125.7, 127.8, 128.5, 129.0, 129.3, 129.3, 133.8, 135.2, 138.9, 163.5 ppm. GC-MS: m/z (%) 333.1 (65) [M$^+$]. IR (KBr): ν 3158, 1567, 1454, 1391, 1329, 1237, 1122, 729, 693, 673, 589, 539, 519, 432 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{19}N_3NaS^+$ 356.1197, found 356.1194.

*1-(3-Methyl-1H-indol-2-yl)-3-(naphthalen-2-ylmethyl)-1H-imidazole-2(3H)-thione (**24d**).* A sample of 169 mg of **22d** was used. Thione **24d** was isolated in 94% yield (174 mg), mp 205 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.13 (s, 3 H, Me), 5.49 (s, 2 H, CH_2), 7.07 (ddd, 1 H, J = 7.9 Hz, J = 7.0 Hz, J = 1.0 Hz), 7.17 (ddd, 1 H, J = 8.2 Hz, J = 7.0 Hz, J = 1.1 Hz), 7.33−7.35 (m, 2 H), 7.44 (d, 1 H, J = 2.5 Hz), 7.50−7.56 (m, 3 H), 7.60 (dd, 1 H, J = 8.2 Hz, J = 1.6 Hz), 7.89−7.95 (m, 4 H), 11.43 ppm (s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 8.1, 50.3, 105.2, 111.3, 118.5, 118.7, 118.8, 119.6, 122.1, 125.9, 126.1, 126.4, 126.6, 127.0, 127.6, 127.7, 128.2 (2 C), 132.4, 132.7, 133.6, 134.2, 164.4 ppm. GC-MS: m/z (%) 369.4 (80) [M$^+$]. IR (KBr): ν 3166, 1602, 1493, 1472, 1403, 1328, 1298, 1242, 1122, 956, 811, 776, 758, 738, 710, 670, 603, 541, 521, 477, 442 cm^{-1}. HR-ESI-MS: calcd for $C_{23}H_{20}N_3S^+$ 370.1378, found 370.1375.

*1-Benzhydryl-3-(3-methyl-1H-indol-2-yl)-1H-imidazole-2(3H)-thione (**24e**).* A sample of 182 mg of **22e** was used. Thione **24e** was isolated in 62% yield (123 mg), mp 201 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.33 (s, 3 H, Me), 6.69 (d, 1 H, J = 2.5 Hz), 6.95 (d, 1 H, J = 2.5 Hz), 7.12−7.16 (m, 1 H), 7.21−7.25 (m, 5 H), 7.33−7.42 (m, 7 H), 7.47 (s, 1 H), 7.56 (d, 1 H, J = 7.8 Hz), 9.59 (br s., 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.9, 64.0, 104.5, 111.5, 116.8, 118.0, 119.0, 120.0, 123.2, 127.8, 128.3, 128.5, 128.6, 128.9, 133.7, 138.3, 163.9 ppm. GC-MS: m/z (%) 395.2 (20) [M$^+$]. IR (KBr): ν 1627, 1489, 1469, 1449, 1397, 1324, 1119, 1095, 1004, 750, 738, 716, 699, 673, 647, 582, 515, 463, 423 cm^{-1}. HR-ESI-MS: calcd for $C_{25}H_{22}N_3S^+$ 396.1534, found 396.1530.

*1-(4-(Dimethylamino)phenyl)-3-(3-methyl-1H-indol-2-yl)-1H-imidazole-2(3H)-thione (**24f**).* A sample of 158 mg of **22f** was used. Thione **24f** was isolated in 54% yield (94 mg), mp 256 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.30 (s, 3 H, Me), 2.94 (s, 6 H, Me_2N), 6.71 (d, 2 H, J = 9.0 Hz), 6.87 (d, 1 H, J = 2.3 Hz), 6.96 (d, 1 H, J = 2.3 Hz), 7.06−7.10 (m, 1 H), 7.14−7.18 (m, 1 H), 7.29 (d, 1 H, J = 8.1 Hz), 7.34 (d, 2 H, J = 9.0 Hz), 7.50 (d, 1 H, J = 8.1 Hz), 9.60 (br s., 1 H,

NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.9, 40.5, 104.7, 111.6, 112.2, 118.3, 119.0, 119.5, 119.9, 123.1, 126.5, 127.0, 127.8, 128.7, 133.9, 150.5, 164.0 ppm. GC-MS: m/z (%) 348.2 (30) [M^+]. IR (KBr): ν 3294, 1738, 1611, 1520, 1489, 1472, 1351, 1330, 1310, 1226, 1194, 1099, 982, 936, 811, 741, 732, 671, 642, 599, 585, 566, 527, 504, 439 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{21}N_4S^+$ 349.1487, found 349.1488.

General Procedure for the Synthesis of the Borane Adducts 26a−g. The ylide (1.0 mmol) and a stirring bar were placed under a nitrogen atmosphere (glovebox) in a bomb tube with 5 equiv excess of 50% triethylborane in hexane (1.5 mL). Then, the tube was closed tightly and placed into a preheated oil bath at 150 °C. The reaction mixture was stirred overnight at that temperature, cooled to room temperature, diluted with THF, and subjected to column chromatography (EtOAC/petroleum ether).

*1-Benzyl-11,11-diethyl-5-methyl-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26a**).* A sample of the ylide **22a** (287 mg, 1.0 mmol) was used. Yield: 238 mg (67%), mp 157 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.55 (t, 6 H, Me), 0.78−0.84 (m, 2 H, CH_2), 0.98−1.04 (m, 2 H, CH_2), 2.53 (s, 3 H, Me), 5.28 (s, 2 H, CH_2), 6.88 (d, 1 H, J = 2.0 Hz), 7.08 (ddd, 1 H, J = 7.9 Hz, J = 6.9 Hz, J = 1.1 Hz), 7.16 (ddd, 1 H, J = 8.0 Hz, J = 6.9 Hz, J = 1.2 Hz), 7.34−7.35 (m, 2 H), 7.45−7.49 (m, 4 H), 7.51 (d, 1 H, J = 2.0 Hz), 7.60 ppm (ddd, 1 H, J = 7.9 Hz, J = 1.2 Hz, J = 0.7 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 8.20, 11.1, 14.3, 52.2, 89.5 112.3, 114.0, 117.3, 118.4, 120.1, 122.0, 128.2, 129.1, 129.3, 131.6, 134.3, 136.0, 136.2, 175.8 ppm. ^{15}N NMR ($CDCl_3$, 60 MHz, $MeNO_2$): δ −218.7, −199.8, −182.3 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3{\cdot}Et_2O$): δ −1.33 ppm. IR (KBr): ν 3445, 2860, 1639, 1488, 1455, 1344, 1235, 1123, 747, 712 cm^{-1}. GC-MS: m/z (%) 355.4 (3) [M^+]. HR-ESI-MS: calcd for $C_{23}H_{27}BN_3^+$ 356.2298, found 356.2298.

*1-(2-Chlorobenzyl)-11,11-diethyl-5-methyl-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26b**).* A sample of **22b** (321 mg) was used. The boron compound **26b** was isolated as white crystals, mp 148 °C, yield 253 mg (65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.38 (t, 6 H, Me, J = 7.4 Hz), 0.62 (q, 1 H, CH_2, J = 7.4 Hz), 0.66 (q, 1 H, CH_2, J = 7.4 Hz), 0.83 (q, 1 H, CH_2, J = 7.4 Hz), 0.87 (q, 1 H, CH_2, J = 7.4 Hz), 2.41 (s, 3 H, Me), 5.32 (s, 2 H, CH_2), 6.86 (d, 1 H, $H_{imidazole}$, J = 2.0 Hz), 6.94 (ddd, 1 H, J = 7.8 Hz, J = 6.9 Hz, J = 1.0 Hz), 7.02 (ddd, 1 H, J = 8.1 Hz, J = 6.9 Hz, J = 1.2 Hz), 7.12 (dd, 1 H, J = 7.6 Hz, J = 1.6 Hz), 7.23 (ddd, 1 H, J = 7.6 Hz, J = 7.6 Hz, J = 1.4 Hz), 7.28 (ddd, 1 H, J = 7.7 Hz, J = 7.6 Hz, J = 1.6 Hz), 7.33 (d, 1 H, J = 8.1 Hz), 7.41−7.43 (m, 2 H), 7.46 (d, 1 H, J = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.2, 11.1, 14.2, 49.6, 89.6, 112.3, 113.9, 117.3, 118.4, 120.1, 122.2, 127.8, 130.1, 130.2, 130.5, 131.5, 132.1, 133.7, 136.0, 136.0, 176.0 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3{\cdot}Et_2O$): δ −1.36 ppm. GC-MS: m/z (%) 360.2 (100) [M − 29]. IR (KBr): ν 2864, 1635, 1485, 1451, 1342, 1136, 1056, 875, 839, 774, 743, 730, 682, 643, 445 cm^{-1}. HR-ESI-MS: calcd for $C_{23}H_{26}BClN_3^+$ 390.1908, found 390.1904.

*11,11-Diethyl-5-methyl-1-(3-methylbenzyl)-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26c**).* A sample of 301 mg of **22c** was used. The boron adduct **26c** was isolated as white crystals, mp 138 °C, yield 114 mg (31%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.55 (t, 6 H, Me, J = 7.4 Hz), 0.79 (q, 2 H, CH_2, J = 7.4 Hz), 0.83 (q, 2 H, CH_2, J = 7.4 Hz), 2.42 (s, 3 H, Me), 2.54 (s, 3 H, Me), 5.26 (s, 2 H, CH_2), 6.91 (d,1 H, $H_{imidazole}$, J = 1.9 Hz), 7.06−7.10 (m, 1 H), 7.15−7.18 (m, 3 H), 7.26 (d, 1 H, J = 7.8 Hz), 7.34−7.38 (m, 1 H), 7.48 (d, 1 H, J = 8.0 Hz), 7.53 (d, 1 H, $H_{imidazole}$, J = 1.9 Hz), 7.60 ppm (d, 1 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.2, 11.1, 14.2, 21.4, 52.2, 89.5, 112.2, 113.9, 117.3, 118.4, 120.0, 122.0, 125.3, 128.9, 129.2, 129.8, 131.6, 134.3, 136.0, 136.2, 139.2, 175.6 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3{\cdot}Et_2O$): δ −1.57 ppm. GC-MS: m/z (%) 369.3 (4) [M^+]. IR (KBr): ν 2864, 1639, 1453, 1343, 1234, 1194, 1122, 1050, 874, 788, 743, 712, 663, 431 cm^{-1}. HR-ESI-MS: calcd for $C_{24}H_{29}BN_3^+$ 370.2455, found 370.2452.

*11,11-Diethyl-5-methyl-1-(naphthalen-2-ylmethyl)-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26d**).* A sample of 337 mg of **26d** was used. The boron adduct **26d** was isolated as white crystals, mp 181 °C, yield 272 mg (67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (t, 6 H, Me), 0.67−0.76 (m, 2 H, CH_2), 0.85−0.95 (m, 2 H, CH_2), 2.39 (s, 3 H, Me), 5.30 (s, 2 H, CH_2), 6.77 (d, 1 H, J = 1.9 Hz), 6.94 (ddd, 1 H, J = 7.9 Hz, J = 7.0 Hz, J = 1.0 Hz), 7.02 (ddd, 1 H, J = 8.3 Hz, J = 7.0 Hz, J = 1.2 Hz), 7.27 (dd, 1 H, J = 8.3 Hz, J = 1.8 Hz), 7.35 (d, 1 H, J = 7.9 Hz), 7.39 (d, 1 H, J = 1.9 Hz), 7.44−7.48 (m, 3 H), 7.68 (s, 1 H), 4.74−7.81 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.2, 11.2, 14.3, 52.4, 66.1, 67.5, 67.7, 89.6, 106.4, 107.7, 112.3, 114.0, 117.3, 118.4, 120.1, 122.0, 125.2, 127.0 (2C), 127.7, 127.9, 128.0, 129.5, 131.6, 131.7, 133.3, 133.3, 136.0, 136.1, 175.7 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3{\cdot}Et_2O$): δ −1.41 ppm. GC-MS: m/z (%) 405.3 (2) [M^+]. IR (KBr): ν 2854, 1172, 1638, 1452, 1337, 1228, 1192, 1123, 1050, 860, 821, 775, 762, 746, 732, 475, 443 cm^{-1}. HR-ESI-MS: calcd for $C_{27}H_{29}BN_3^+$ 406.2455, found 406.2450.

*1-Benzhydryl-11,11-diethyl-5-methyl-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26e**).* A sample of 321 mg of **22e** was used. The boron adduct **26e** was isolated as white crystals, mp 33 °C, yield 362 mg (84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.31 (t, 6 H, Me, J = 7.7 Hz), 0.58−0.67 (m, 2 H, CH_2), 0.86−0.94 (m, 2 H, CH_2), 2.47 (s, 3 H, Me), 6.86 (s, 1 H), 6.90 (d, 1 H, J = 2.0 Hz), 6.98−7.02 (m, 1 H), 7.06−7.10 (m, 1 H), 7.18−7.21 (m, 4 H), 7.35−7.42 (m, 7 H), 7.51−7.53 ppm (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.2, 10.9, 14.2, 65.8, 89.6, 112.2, 113.7, 117.3, 118.4, 120.1, 121.4, 128.2, 128.9, 129.1, 131.6, 136.0, 136.1, 138.0 ppm. ^{11}B NMR ($CDCl_3$. 128 MHz, $BF_3{\cdot}Et_2O$): δ −1.29 ppm. GC-MS: m/z (%) 431.2 (1.5) [M^+]. IR (KBr): ν 2858, 1635, 1452, 1341, 1209, 1030, 722, 695, 657 cm^{-1}. HR-ESI-MS: calcd for $C_{29}H_{31}BN_3^+$ 432.2611, found 432.2602.

*1-(4-(Dimethylamino)phenyl)-11,11-diethyl-5-methyl-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26f**).* A sample of 316 mg of **22f** was used. The boron adduct **26f** was isolated as white crystals, mp 192 °C, yield 300 mg (78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.37 (t, 6 H, J = 7.6 Hz), 0.50−0.60 (m, 2 H, CH_2), 0.77−0.87 (m, 2 H, CH_2), 3.03 (s, 6 H, NMe_2), 6.77 (d, 2 H, J = 9.0 Hz), 7.01 (ddd, 1 H, J = 7.8 Hz, J = 7.0 Hz, J = 1.1 Hz), 7.08 (ddd, 1 H, J = 8.0 Hz, J = 7.0 Hz, J = 1.3 Hz), 7.18 (d, 1 H, J = 1.8 Hz), 7.34 (d, 2 H, J = 9.0 Hz), 7.40 (d, 1 H, J = 8.0 Hz), 7.55 (d, 1 H, J = 7.8 Hz), 7.59 ppm (d, 1 H, J = 1.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.3, 10.9, 14.7, 40.4, 89.4, 112.2, 112.3, 113.4, 117.2, 118.4, 119.9, 123.6, 124.7, 125.8, 131.6, 135.8, 136.1, 150.8 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3{\cdot}Et_2O$): δ −0.01 ppm. IR (KBr): ν 2858, 1739, 1640, 1612, 1521, 1451, 1335, 1227, 1138, 1035 884, 821, 742, 717, 694, 670, 642, 564, 529, 443 cm^{-1}. HR-ESI-MS: calcd for $C_{24}H_{30}BN_4^+$ 385.2564, found 385.2560.

*1-Benzyl-5-methyl-11,11-diphenyl-1,11-dihydroimidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide (**26g**).* A sample of 287 mg of **22a** and 726 mg (3 equiv) of triphenylborane was used. The boron adduct **26g** was isolated as white crystals, mp 244 °C, yield 190 mg (42%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.60 (s, 3 H, Me), 5.21 (s, 2 H, CH_2), 6.76−6.77 (m, 1 H), 6.91−6.93 (m, 2 H), 7.09−7.11 (m, 2 H), 7.26−7.49 (m, 16 H), 7.64−7.65 ppm (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.2, 52.5, 91.2, 112.9, 114.0, 117.9, 118.6, 121.0, 122.4, 126.1, 127.7, 128.7, 129.1, 129.2, 131.9, 133.6, 134.0, 135.4, 135.9, 147.0, 171.8 ppm. ^{15}N NMR ($CDCl_3$, 60 MHz, $MeNO_2$): −278.5, −204.2, −188.6 ppm. ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3{\cdot}Et_2O$): δ −2.60 ppm. GC-MS: m/z (%) 451.2 (30) [M^+]. IR (KBr): ν 1644, 1495, 1453, 1343, 1266, 1174, 992, 868, 745, 730, 703, 596, 442 cm^{-1}. HR-ESI-MS: calcd for $C_{31}H_{27}BN_3^+$ 452.2298, found 452.2296.

2-(1-Benzyl-1*H*-imidazolium-3-yl)-3-methylindolate (27). Benzylimidazole (211 mg; 1.3 mmol) and 3-methylindole (145 mg, 1.0 mmol) were used. 1-Benzyl-2-methyl-3-(3-methyl-1*H*-indol-2-yl)imidazolium bromide was isolated as colorless crystals, mp 242.3 °C, yield 336 mg (88%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.18 (s, 3 H, Me_{indole}), 2.59 (s, 3 H, $Me_{imidazole}$), 5.60 (s, 2 H, CH_2), 7.16 (dd, 1 H, J = 7.7 Hz, J = 7.3 Hz), 7.28 (dd, 1 H, J = 8.1 Hz, J = 7.3 Hz), 7.42 − 7.51 (m, 6 H), 7.66 (d, 1 H, J = 7.7 Hz), 8.09 (s, 1 H), 11.84 ppm (br s, 1 H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.5, 10.4, 51.3, 106.9, 111.8, 119.6, 119.8, 122.4, 123.6, 123.9, 123.9, 126.5, 128.0,

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128.7, 129.1, 133.7, 134.1, 146.6 ppm. ESI-MS: m/z (%) 302.1 [M^+]. IR (KBr): ν 3048, 1582, 1493, 1452, 1332, 1177, 1009, 743, 734, 699, 664, 631, 468, 428 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{20}N_3^+$ 302.1657, found 302.1656.

A sample of 382 mg of 1-benzyl-2-methyl-3-(3-methyl-1*H*-indol-2-yl)imidazolium bromide was used to prepare the ylide as described before. The ylide **27** was isolated as a yellowish powder, mp 98.0 °C, yield 253 mg (84%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.14 (s, 3 H, Me_{indole}), 2.58 (s, 3 H, $Me_{imidazole}$), 5.50 (s, 2 H, CH_2), 6.74 (dd, 1 H, $J_1 \approx J_2$ = 7.4 Hz), 6.81 (dd, 1 H, $J_1 \approx J_2$ = 7.4 Hz), 7.25 (d, 1 H, J = 8.0 Hz), 7.34 (d, 1 H, 7.8 Hz), 7.39−7.49 (m, 5 H), 7.80 (d, 1 H, J = 2.0 Hz), 7.84 ppm (d, 1 H, J = 2.0 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 8.7, 10.3, 50.8, 97.5, 115.2, 116.2, 117.3, 117.7, 121.2, 123.2, 127.8, 128.5, 129.1, 129.4, 134.5, 135.3, 142.0, 144.2 ppm. ESI-MS: m/z (%) 302.1 [M + H^+]. IR (KBr): ν 3060, 1395, 1323, 1288, 733, 694, 440 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{20}N_3^+$ 302.1657, found 302.1658.

1-Benzyl-3-(1,3-dimethyl-1*H*-indol-2-yl)imidazolium Bromide (29). Benzylimidazole (211 mg; 1.3 mmol) was used. The salt **29** was isolated as colorless crystals, mp 234.0 °C, yield 279 mg (73%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.20 (s, 3 H, Me), 3.60 (s, 3 H, NMe), 5.62 (s, 2 H, CH_2), 7.20 (dd, 1 H, $J_1 \approx J_2$ = 7.6 Hz), 7.36 (dd, 1 H, $J_1 \approx J_2$ = 7.6 Hz), 7.42−7.51(m, 3 H), 7.55−7.60 (m, 3 H), 7.69 (d, 1 H, J = 8.0 Hz), 8.16−8.18 (m, 1 H), 8.21−8.23 (m, 1 H), 9.96 ppm (br s, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 7.6, 29.4, 52.5, 106.5, 110.4, 119.6, 120.1, 123.3, 123.8, 125.1, 125.3, 125.8, 128.4, 128.9, 129.1, 134.3, 134.7, 138.9 ppm. ESI-MS: m/z (%) 302.1 [M^+]. IR (KBr): ν 2947, 1564, 1456, 1368, 1271, 1193, 1106, 908, 763, 752, 723, 662, 615, 549, 463, 411 cm^{-1}. HR-ESI-MS: calcd for $C_{20}H_{20}N_3^+$ 302.1657, found 302.1655.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and a CIF file giving additional compound characterization data, X-ray data, results of calculations, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: schmidt@ioc.tu-clausthal.de.

Notes

The authors declare no competing financial interest.

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