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Chiral N-Heterocyclic Carbene Borane Complexes: Synthesis and Structural Analysis

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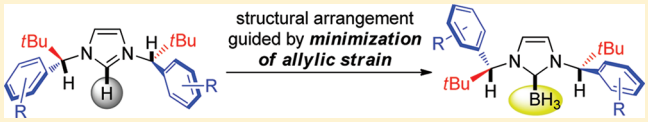
Supporting Information

ABSTRACT: A new family of chiral N-heterocyclic carbene borane complexes was synthesized starting from their corresponding imidazolium salts. The complexes were fully characterized. X-ray crystal structures of the complexes were obtained.



INTRODUCTION

Since Arduengo's report of the first persistent N-heterocyclic carbene (NHC),[1] NHCs have become of paramount importance in the field of catalysis. Due to their versatility, tunable steric and electronic properties, and ease of formation of metal complexes, NHCs have found extensive utility in transition metal catalyzed[2,3] and organocatalytic reactions.[4] Only slowly, however, do chiral NHC ligands make their way into the realm of asymmetric catalytic reactions that provide products with high asymmetric induction, and in a number of routes of access, chiral ligands have to be separated by high-performance liquid chromatography on a chiral phase.[5,6] Successful reactions (product er ≥ 95:5) include olefin metathesis,[7−10] 1,4-addition of arylboronic acids to enones,[11] hydrosylilation of ketones,[12] intramolecular α-arylation of amides to give 3-disubstituted oxindoles,[13−18] copper-catalyzed conjugate addition to cyclic ennones,[19,20] nickel-catalyzed reductive coupling of 1,3-dienes and aldehydes with triethylsilane,[21] copper-catalyzed allylic arylation with aryl Grignard reagent,[22] copper-catalyzed addition of arylboronates to isatins,[23] rhodium-catalyzed hydroarylation of azabicycles,[24] ruthenium-catalyzed hydrogenation of quinoxalines,[25] and palladium-catalyzed alkane activation to give fused indolines.[26]

The strategies that have been developed to introduce chirality in the NHC's can be categorized as (a) chirality in the N-heterocyclic backbone,[7,27−29] (b) chirality in the N-substituents,[30−33] and (c) a combination of the above two.[19,34,35]

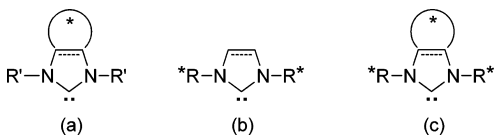
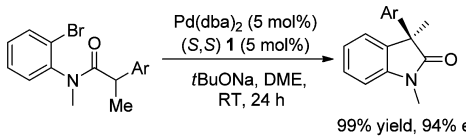


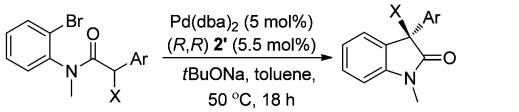
Figure 1. Source of chirality in NHCs.

Our laboratory has focused on NHC ligands with chiral N-substituents incorporating *o*-substituted phenyl or 1-naphthyl groups (Figure 2).

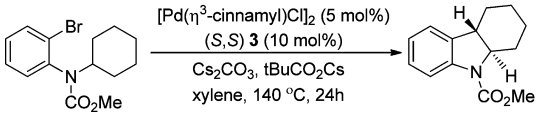
Ligand **1** was shown to be the best in the Pd-catalyzed intramolecular arylation of amides to give 3,3-disubstituted chiral oxindoles (eq 1).[13,18] **2′** was the ligand of choice for the



99% yield, 94% ee (1)



X = OR, 89% yield, 96% ee
X = NR_2, 96% yield, 90% ee (2)



84% yield, 95% ee (3)

synthesis of chiral oxindoles having a 3-alkoxy or 3-amino group at the stereogenic center (eq 2).[14] Ligand **3** provided excellent results in Pd-catalyzed C−H activation of unactivated methylene groups, leading to the formation of fused indolines with high enantioselectivity (eq 3).[26]

We hypothesized that minimization of allylic strain sets the stereocontrol elements of the catalyst in place and brings about such high stereoselectivity.[18,26] This, and the high thermal stability of the Pd-NHC system, significantly extends the range of successful applications in catalysis. We sought to increase our knowledge of the solid-state structure of complexes incorporating these ligands, and our choice fell on NHC−borane adducts for this study.

Recently, NHC complexes of main group elements such as NHC−boranes are gaining importance.[36−55] Experimental

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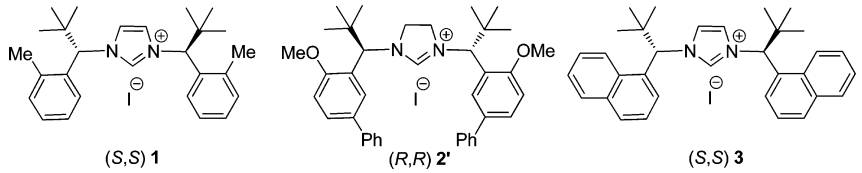
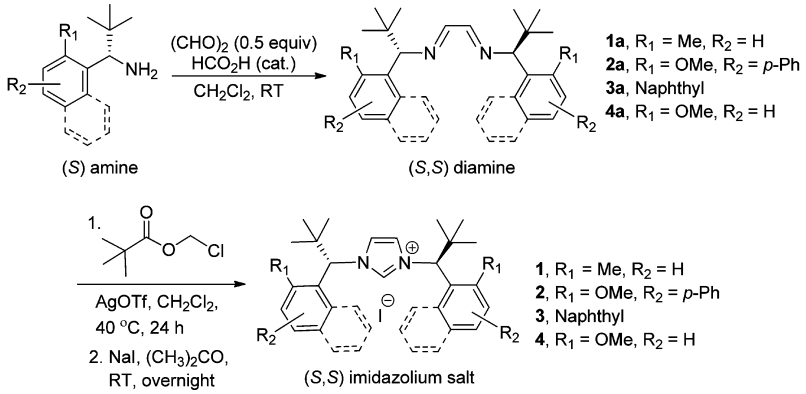
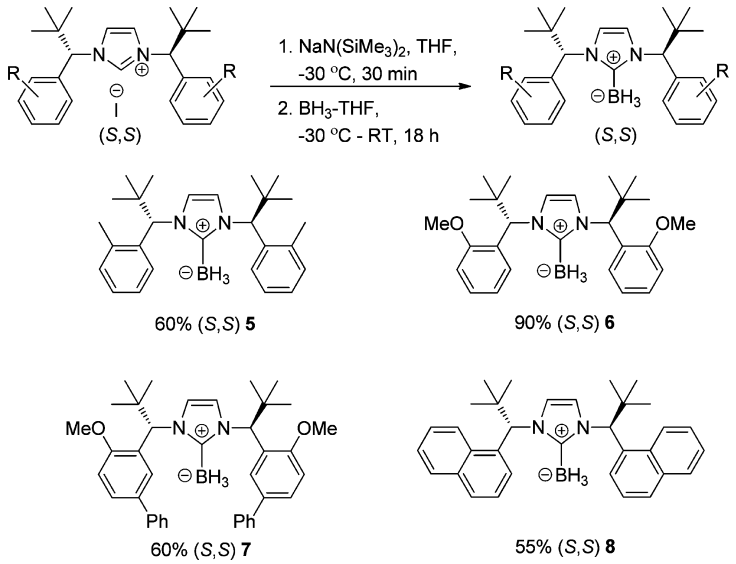


Figure 2. NHC ligands developed in our group.

Scheme 1. Synthesis of Imidazolium Salts



Scheme 2. Synthesis of NHC−BH_3 Complexes



results along with DFT calculations on NHC−boranes have shown recently that coupling of an NHC with BH_3 changes the electronic properties of the borane considerably.[56,57] In an NHC−BH_3 complex, the B−H bond is weakened due to the π-conjugation with the carbene ligand, and this results in a much lower bond energy of the B−H bond (74−80 kcal/mol) compared to that of BH_3 (106 kcal/mol).[56] Therefore, unlike boranes, NHC−boranes act as radical hydrogen donors.[56−58] Applications of the NHC−boranes were then followed in the radical reduction of xanthates,[56−58] ionic reduction of halides,[59] Suzuki−Miyaura cross-coupling reactions,[60] and reduction of ketones.[61] NHC−boranes and their derivatization and applications have been recently reviewed.[62] However, examples of chiral NHC−borane complexes derived from chiral NHC ligand precursors are scarce.[61−63]

Here we report on the synthesis and structures of sterically demanding chiral N-heterocyclic carbene borane complexes incorporating successful ligands for the reactions shown in eqs 1−3.

■ RESULTS AND DISCUSSION

The imidazolium salts **1**−**4** were employed in the synthesis of new NHC−borane complexes. They were obtained from the corresponding chiral amines, which in turn were prepared by literature-known procedures (see Experimental Details for details).[13,14,26] The chiral amines were condensed with glyoxal to provide the corresponding chiral diimines **1a**−**4a**.[13,14,26] The diimines were then reacted with chloromethylpivalate in the presence of silver triflate to obtain the imidazolium triflates.[64] Anion metathesis to the corresponding iodides was carried out

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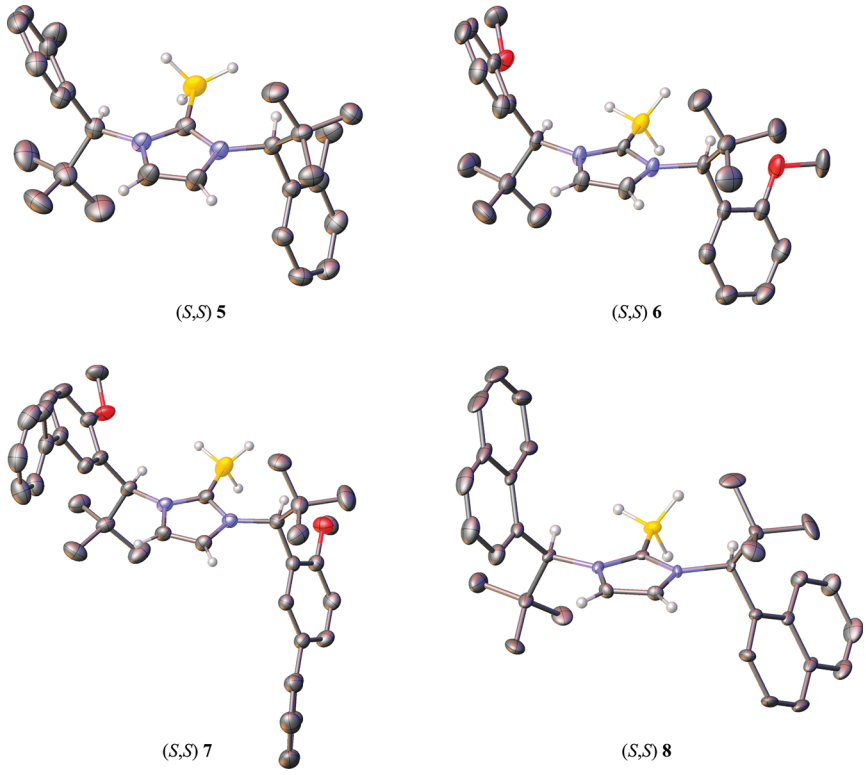

Figure 3. ORTEP diagram of complexes **5**–**8** (50% probability level for the thermal ellipsoids). Hydrogen atoms of the aromatic rings and methyl groups have been removed for clarity.

because the iodide salts were solids and easier to purify (Scheme 1).[13,14,26]

Deprotonation of the imidazolium salts followed by the reaction with BH_3 was the route chosen to access complexes **5**–**8**. Screening bases such as NaH, KO*t*Bu, and sodium hexamethyldisilazide (NaHMDS) proved NaHMDS to be the best base. The *in situ* generated carbenes were then quenched with BH_3–THF. The NHC–borane complexes were isolated by flash column chromatography in moderate to excellent yields (55–90%) (Scheme 2).

The white, crystalline, air- and moisture-stable complexes **5**–**8** have melting points > 200 °C. They were characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. Consistent with analogous, previously reported complexes,[62] ^{1}H NMR signals for the B–H protons appear in the range 1.8–0.8 ppm as a quartet reflecting the coupling with the ^{11}B nucleus. In the ^{13}C NMR spectra of previously reported NHC–BH_3 complexes, the carbene carbon was observed in the range δ = 153.3–186.0 ppm.[62] In case of complexes **5**–**8** the ^{13}C NMR spectra reveal the presence of a broad multiplet between δ = 174.5 and 176.7 ppm that corresponds to the quaternary N–C–N carbon atom. The signal is broadened due to coupling with the quadrupolar boron nuclei of spin 3 (^{10}B) and 3/2 (^{11}B), respectively. Further analysis of 2D-NMR spectra clearly shows the correlation between the carbene carbon (N–C–N) and the neighboring protons (for details see the Supporting Information). In the case of the imidazolium salts the N–CH–N carbon atoms appear in the ^{13}C NMR spectra below 150 ppm, whereas the change of electronic environment around the carbene carbon atom (N–C–N) in an NHC–BH_3 complex results in a downfield shift of the signal (above 170 ppm). The ^{11}B NMR resonances of the literature-known NHC–boranes appear between δ = −32 and −38 ppm.[62] The proton-decoupled ^{11}B resonances of complexes **5**–**8** exhibit broad singlets in the range 33–37 ppm, values that lie in between those for amine–borane and phosphine–boranes adducts.[65,66]

Crystals of complexes **5**–**8** suitable for X-ray diffraction were grown by vapor diffusion of hexane into a CH_2Cl_2 solution.

In the solid-state structures of **5**–**8** (Figure 3), the three-dimensional arrangements of the substituents at the stereogenic centers are guided by the minimization of allylic strain ($A^{1,3}$-strain). Consequently, an approximate coplanarity of the C–H bonds at the stereogenic centers and the C(ligand)–B bond is found in all complexes. This places the *t*Bu groups and the aryl groups at the two stereogenic centers in opposite hemispheres. The *ortho*-substituents on the aryl (or the naphthyl ring in the case of complex **8**) are again close to coplanar with the C–H bonds at the stereogenic centers since any rotation around the C(aryl)–C(stereogenic center) bond would lead to an increase in $A^{1,3}$-strain except one of 180°, but then the *o*-aryl substituent would enter into conflict with the *t*Bu group.

In comparison with the crystal structure of the carbene ligand precursor (Figure 4), the *t*Bu groups are lying in one hemisphere and the aryl groups are lying in the other with respect to the heterocycle plane. The rotational change in the

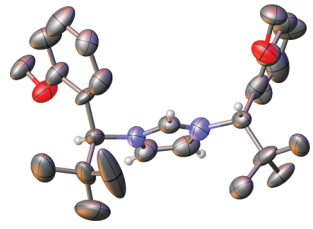

Figure 4. ORTEP diagram of imidazolium salt **4** (50% probability level for the thermal ellipsoids). Iodine atom has been removed for clarity.

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case of the carbene complexes is as expected when considering the minimization of $A_{1,3}$-strain. The anti-arrangement of the *t*Bu groups is also found in the structures of an NHC palladium complex.[18,26]

Further details of the structural features of the borane complexes emerge when comparing, the pairs of molecules having similar functional groups, namely, complexes **5** and **8** and complexes **6** and **7**.

In **5** there are three independent molecules per asymmetric unit. As shown in Figure 5a, **5B** and **5C** are almost perfectly superimposable (rms 0.183 Å for all atoms), whereas **5A** is slightly different (rms AC 0.704 Å and AB 0.788 Å for all atoms), in particular in the arrangement of the aryl ring bearing carbon atoms C20−C25. This is clearly reflected in the values of the torsion angles C2−N3−C19−C20 and N3−C19−C20-C25 (see Table 1).

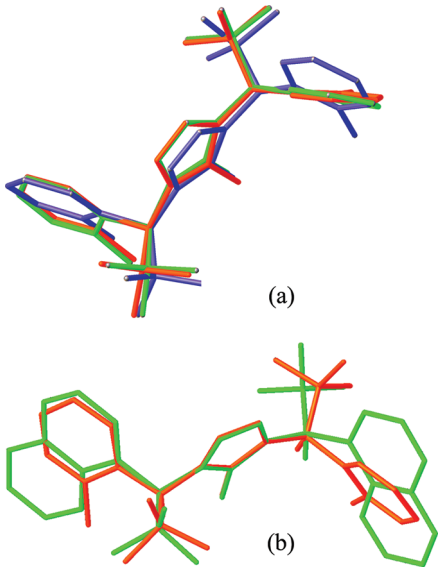

Figure 5. (a) Overlap of the three independent molecules present in the unit cell of **5** (A: blue; B: orange C: green); (b) overlap of **5B** (orange) and **8** (green).

In **8** there is only one molecule present per asymmetric unit. Figure 5b represents the superimposed structure of **5B** and **8**. The presence of three different molecules in one asymmetric unit of **5** makes the comparison with **8** difficult. In Table 1, entries 11−14 show the relative position of the H atom at the stereogenic center with respect to the C(stereogenic center)−B and C(aromatic)−CH_3 bonds. It emerges that the structural differences between **5** and **8** are not larger than that of the three independent molecules in **5**.

In **6** there are two independent molecules in the asymmetric unit. However, contrary to what is observed in **5**, the molecular geometry of **6** is more rigid and the two independent molecules in the asymmetric unit adopt very similar conformations (Figure 6a).

In the superposed picture of **6** and **7** (Figure 6b), it is clear that the common parts of **6** and **7** also adopt very similar geometries. The main difference lies in the orientation of one of the aryl rings.

Variation of torsion angles in the solid-state structures of **5**−**8** have been displayed in Table 1. It reflects the arrangements of different substituents at the stereogenic centers of the molecules.

As shown in Table 1, the values of the torsion angles of the three molecules in complex **5** are very different, which reflects the flexible molecular geometry of **5**. In contrast, in complex **6** the values of the torsion angles of the two independent molecules are close to each other. This may result from a stabilized geometry of the molecule due to the interaction between the BH_3 moiety and the OMe− groups in complex **6**. In the case of **7** and **8** there is only one molecule present per asymmetric unit.

To quantify the steric bulk of the ligands, the buried volumes (%V_{bur}) of the complexes **5**−**8** were calculated (Table 2).[67,68]

CONCLUSION

A series of new chiral NHC−borane complexes are reported. Crystal structures of the complexes convincingly show the importance of allylic strain in the arrangement of the ligands' substituents in space.

EXPERIMENTAL DETAILS

General Methods. Experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with a Solvtek system. For the synthesis of NHC−boranes, THF was degassed by two pump−freeze−thaw cycles. All commercially available compounds were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories. NMR spectra were recorded on

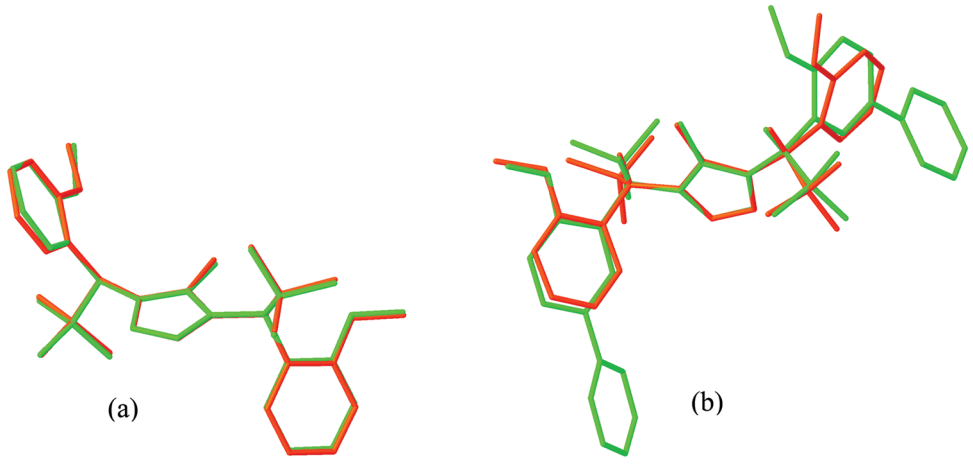

Figure 6. (a) Overlap of the two independent molecules present in the unit cell of complex **6** (A: orange; B: green); (b) overlap of **6A** (orange) and **7** (green).

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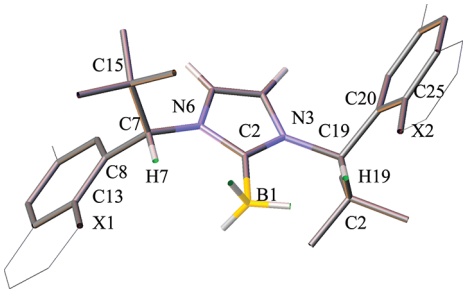
Table 1. Comparison of Selected Torsion Angles (deg) in Complexes 5−8



entry		(*S*,*S*)-**5**	(*S*,*S*)-**8**	(*S*,*S*)-**6**	(*S*,*S*)-**7**
1	C2−N6−C7−C8	−106.3(2) −99.4(3) −110.0(3)	−109.9(3)	−102.5(2) −107.5(2)	−117.7(2)
2	C2−N3−C19−C20	−132.6(2) −105.4(3) −100.1(3)	−127.9(3)	−113.9(2) −115.0(2)	−108.5(2)
3	C2−N6−C7−C15	121.5(2) 128.8(2) 117.2(3)	117.1(3)	126.4(2) 121.6(2)	109.1(2)
4	C2−N3−C19−C27	99.9(3) 121.5(3) 127.6(3)	98.8(4)	114.3(2) 113.4(2)	118.7(2)
5	N3−C19−C20−C25	100.1(2) 130.3(2) 126.6(3)	118.7(2)	132.10(19) 128.8(2)	118.7(2)
6	N6−C7−C8−C13	125.2(3) 127.4(2) 121.9(3)	132.6(2)	140.54(19) 141.41(18)	132.6(2)
7	C2−N6−C7−H7	7 14 3	4	12 7	−4
8	C2−N3−C19−H19	−20 8 13	−15	0 −1	5
9	C7−N6−C2−B1	−2.7(4) −5.8(4) −7.2(4)	6.4(3)	6.4(3) 3.0(3)	0.3(5)
10	C19−N3−C2−B1	6.2(4) 5.7(4) 8.0(4)	−0.5(3)	−3.5(3) 1.2(3)	−1.9(5)
11	B1−C2−C7−H7	1 9 1	4	17 9	1
12	B1−C2 C19−H19	−15 15 18	−17	−2 0	4
13	X1−C13−C7−H7	(X1 = C14) 11 11 9	(X1 = C36) 19	(X1 = O14) 23 23	(X1 = O14) 18
14	X2−C25−C19−H19	(X2 = C26) −11 16 15	(X2 = C35) −6	(X2 = O26) 19 16	(X2 = O26) 6

Bruker AMX 500 and AMX 400 spectrometers at ambient probe temperature. IR spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. Melting points were measured using a Büchi 510 apparatus. $[\alpha]_D$ values were recorded on a Perkin-Elmer 241 polarimeter using a quartz cell (l = 10 cm) and a Na high-pressure lamp (λ = 589 nm).

Table 2. Calculation of %V_{bur}[a]

entry	complexes	%V_{bur}
1	**5**	35.4
2	**6**	31.8
3	**7**	36.6
4	**8**	36.4

[a]Calculated using SambVca with the standard parameters: radius of sphere 3.5 Å, distance from sphere 2.1 Å, mesh step 0.05 Å.[67].

Synthesis of the Imidazolium Salts. The imidazolium salts **1**,[13] **3**,[26] and **4**[13] were synthesized following literature procedures. The synthesis of the diimine **2a** (see Scheme 1) was previously reported.[14]

1,3-Bis((*S*)-1-(4-methoxy-[1,1′-biphenyl]-3-yl)-2,2-dimethylpropyl)-1*H*-imidazol-3-ium Iodide (2). Chloromethyl pivalate (376 mg, 2.50 mmol, 1.5 equiv) was added to silver triflate (642 mg, 2.50 mmol, 1.5 equiv) in CH_2Cl_2 (13 mL) in a Schlenk tube, and the mixture was stirred at rt for 45 min in the dark. The resulting suspension was transferred via cannula equipped with a filter into a dry Schlenk tube containing the diimine **2a** (938 mg, 1.67 mmol). The resulting mixture was stirred at 40 °C for 24 h in the dark. After cooling to rt, the reaction mixture was dried.

The crude material was redissolved in acetone (17 mL), and sodium iodide (2.5 g, 16.7 mmol, 10 equiv) was added. The mixture was stirred at rt overnight. The solvent was evaporated, and the residue was taken up in a minimum amount of chloroform and filtered though a cotton plug. After concentrating, the filtrate was submitted to a second cycle of anion exchange. Finally flash column chromatography using CH_2Cl_2/Et_2O (1:1) as eluent afforded the pure imidazolium salt **2** (468 mg, 40%) as a yellowish-brown powder: mp = 157 °C; $[\alpha]^{20}_D$ = −127 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H, NC*H*N), 7.90 (d, J = 1.9 Hz, 2H, CH_{arom}), 7.57−7.54 (m, 6H, CH_{arom}), 7.45−7.39 (m, 6H, CH_{arom}), 7.34−7.30 (m, 2H, CH_{arom}), 6.96 (d, J = 8.6 Hz, 2H, C$H_{olefinic}$), 6.30 (s, 2H, C*H*), 3.86 (s, 6H, OCH_3), 1.21 (s, 18H, C$(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (s, C_{arom}), 139.9 (s, C_{arom}), 138.6 (s, NCHN), 133.5 (s, C_{arom}), 128.9 (s, C_{arom}), 127.8 (s, C_{arom}), 127.1 (s, C_{arom}), 126.8 (s, C_{arom}), 123.8 (s, C_{arom}), 121.5 (s, C_{arom}), 111.9 (s, $C_{olefinic}$), 66.3 (s, C*H*), 55.9 (s, OCH_3), 36.1 (s, C$(CH_3)_3$), 27.9 (s, C$(CH_3)_3$); IR (ν, cm^{-1}) 3773, 3715, 2962, 1486, 1255, 1142, 762; HRMS (ESI, m/z) calcd for $C_{39}H_{45}N_2O_2$ ([M − I]$^+$):573.3475, found 573.3486. Anal. Calcd for $C_{39}H_{45}IN_2O_2$: C, 66.85; H, 6.47; N, 4.00. Found: C, 66.71; H, 6.77; N, 3.76.

General Procedure for the Synthesis of the NHC−Borane Complexes. The imidazolium salt (1 equiv, 0.5 mmol) was placed in a flame-dried Schlenk tube. Dry, degassed THF (3 mL) was added. The suspension was cooled to −30 °C, and NaHMDS (1.2 equiv, 0.6 mmol, 2 M solution in THF) was added. The mixture was then stirred for 30 min at −30 °C followed by the addition of BH_3−THF (3 equiv, 1.5 mmol, 1 M solution in THF) at the same temperature. The reaction was warmed to rt over an 18 h period. Volatiles were evaporated under vacuum, and the mixture was redissolved in CH_2Cl_2 (2 mL) and filtered through a short pad of Celite. The Celite was washed with CH_2Cl_2, and the filtrate was concentrated. The crude material was dissolved in a minimum amount of CH_2Cl_2, and silica (same in amount compared to the crude material) was added. The mixture was taken to dryness in a Rotavapor to get free-flowing powder. This was loaded onto a silica gel column, and the product was eluted using 15−20% EtOAc in cyclohexane.

(1,3-Bis((*S*)-2,2-dimethyl-1-(*o*-tolyl)propyl-1*H*-imidazol-3-ium-2-yl) Trihydroborate (5). Following the general procedure complex **5** (121 mg, 60%) was obtained after purification by flash chromatography on silica gel using 15% EtOAc in cyclohexane: mp = 278 °C; $[\alpha]^{20}_D$ = −12.02 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H, CH_{arom}), 7.32 (s, 2H, C$H_{olefinic}$), 7.21−7.18 (m, 6H, CH_{arom}), 6.44 (s, 2H, C*H*), 2.62 (s, 6H, CH_3), 1.01 (s, 18H, C$(CH_3)_3$), 1.62−1.01 (m, BH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5−174.4 (bm, NCN), 139.1(s, C_{arom}), 136.7 (s, C_{arom}), 131.5 (s, C_{arom}), 128.1 (s, C_{arom}), 127.5 (s, C_{arom}), 125.2 (s, C_{arom}), 118.3 (s,

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Table 3. Crystallographic Data for Complexes 5−8

	5	6	7	8
chemical formula	$C_{27}H_{39}BN_2$	$C_{27}H_{39}BN_2O_2$	$C_{39}H_{47}BN_2O_2$	$C_{33}H_{39}BN_2$
formula mass	402.41	434.41	586.60	474.47
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
a/Å	46.4335(19)	12.55564(15)	7.4531(6)	20.7759(8)
b/Å	7.3273(2)	14.24537(18)	17.8577(5)	7.1727(3)
c/Å	23.5143(10)	14.6874(2)	26.0300(15)	19.0739(6)
α/deg	90.00	90.00	90.00	90.00
β/deg	110.669(3)	98.7154(12)	90.00	106.583(4)
γ/deg	90.00	90.00	90.00	90.00
unit cell volume/Å^3	7485.4(5)	2596.65(6)	3464.5(3)	2724.16(18)
temperature/K	180.0	180.15	180.15	189.9
space group	$C2$	$P2$	$P2_12_12_1$	$C2$
no. of formula units per unit cell, Z	12 (Z'=3)	4 (Z'=2)	4	4
radiation type	Mo Kα	Cu Kα	Cu Kα	Cu Kα
absorp coeff, μ/mm^{-1}	0.061	0.531	0.523	0.496
no. of reflns measd	27 046	20 141	8958	5481
no. of indep reflns	7932	5393	3829	2635
R_{int}	0.0664	0.0392	0.0300	0.0463
final R_1 values ($I > 2\sigma(I)$)	0.0464	0.0440	0.0398	0.0542
final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1060	0.1214	0.1129	0.1336
final R_1 values (all data)	0.0551	0.0494	0.0446	0.0681
final $wR(F^2)$ values (all data)	0.1098	0.1264	0.1183	0.1448
goodness of fit on F^2	1.057	1.031	0.910	1.035

$C_{olefinic}$), 64.4 (s, *C*H), 37.6 (s, *C*(CH$_3$)$_3$), 28.1 (s, C(*C*H$_3$)$_3$), 21.5 (s, *C*H$_3$); ^{11}B NMR (CDCl$_3$, 96.3 MHz) δ −33.16; IR (ν, cm^{-1}) 3744, 3686, 2972, 2357, 2055, 1264, 731; HRMS (ESI, m/z) calcd for $C_{27}H_{36}BN_2$ ([M − 3H]$^+$) 399.2966, found 399.2962. Anal. Calcd for $C_{27}H_{39}BN_2$: C, 80.58; H, 9.77; N, 6.96. Found: C, 80.16; H, 10.18; N, 6.94.

(1,3-Bis((*S*)-1-(2-methoxyphenyl)-2,2-dimethylpropyl)-1*H*-imidazol-3-ium-2-yl) Trihydroborate (6). According to the general procedure and after purifying by flash chromatography on silica gel using 20% EtOAc in cyclohexane complex **6** (195 mg, 90%) was obtained: mp = 229 °C; $[\alpha]^{20}_D$ = +32.17 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.1, 1.7 Hz, 2H, C*H*$_{arom}$), 7.34 (s, 2H, C*H*$_{olefinic}$), 7.27−7.23 (m, 2H, C*H*$_{arom}$), 6.92−6.89 (m, 4H, C*H*$_{arom}$), 6.76 (s, 2H, *CH*), 3.86 (s, 6H, *CH*$_3$), 0.93 (s, 18H, C(*CH*$_3$)$_3$), 1.48−0.93 (m, B*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4−175.3 (bm, NCN), 158.0 (s, C_{arom}), 129.3 (s, C_{arom}), 128.6 (s, C_{arom}), 126.9 (s, C_{arom}), 119.7 (s, C_{arom}), 118.1 (s, $C_{olefinic}$), 111.7 (s, C_{arom}), 61.8 (s, *CH*), 55.8 (s, OCH$_3$), 36.7 (s, *C*(CH$_3$)$_3$), 27.9 (s, C(*C*H$_3$)$_3$); ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ −36.16; IR (ν, cm^{-1}) 3570, 3521, 2961, 2338, 2282, 1492, 1462, 1241, 760; HRMS (ESI, m/z) calcd for $C_{27}H_{38}BN_2O_2$ ([M − H]$^+$) 433.3020, found 433.3025. Anal. Calcd for $C_{27}H_{39}BO_2N_2$: C, 74.65; H, 9.05; N, 6.45. Found: C, 74.12; H, 9.28; N, 6.43.

(1,3-Bis((*S*)-1-(4-methoxy-[1,1′-biphenyl]-3-yl)-2,2-dimethylpropyl)-1*H*-imidazol-3-ium-2-yl) Trihydroborate (7). Following the general procedure complex **7** (176 mg, 60%) was obtained after purification by flash chromatography on silica gel using 15% EtOAc in cyclohexane: mp = 294 °C; $[\alpha]^{20}_D$ = −79.78 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 4.8 Hz, 2H, C*H*$_{arom}$), 7.52−7.42 (m, 12H, C*H*$_{arom}$), 7.34−7.31 (m, 2H, C*H*$_{arom}$), 6.99 (d, J = 8.6 Hz, 2H, C*H*$_{arom}$), 6.80 (s, 2H, *CH*) 3.91 (s, 6H, OC*H*$_3$), 1.03 (s, 18H, C(*CH*$_3$)$_3$), 1.59−1.03 (m, B*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7−175.7 (bm, NCN), 157.6 (s, C_{arom}), 141.1 (s, C_{arom}), 132.9 (s, C_{arom}), 128.8 (s, C_{arom}), 128.4 (s, C_{arom}), 127.4 (s, C_{arom}), 127.2 (s, C_{arom}), 126.8 (s, C_{arom}), 126.7 (s, C_{arom}), 118.3 (s, $C_{olefinic}$), 112.0 (s, C_{arom}), 62.3 (s, *CH*), 56.0 (s, OCH$_3$), 36.8 (s, *C*(CH$_3$)$_3$), 28.0 (s, C(*C*H$_3$)$_3$); ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ −34.31; IR (ν, cm^{-1}) 3750, 2254, 903, 722; HRMS (ESI, m/z) calcd for $C_{39}H_{46}BN_2O_2$ ([M − H]$^+$) 585.3646, found 585.3641.

(1,3-Bis((*S*)-2,2-dimethyl-1-(naphthalene-1-yl)propyl)-1*H*-imidazol-3-ium-2-yl) Trihydroborate (8). According to the general procedure and after purifying by flash chromatography on silica gel using 15% EtOAc in cyclohexane complex **8** (130 mg, 55%) was synthesized: mp = 225 °C; $[\alpha]^{20}_D$ = +80.50 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.7 Hz, 2H, C*H*$_{arom}$), 7.85−7.82 (m, 6H, C*H*$_{arom}$), 7.63−7.60 (m, 2H, C*H*$_{arom}$), 7.52−7.46 (m, 4H, C*H*$_{arom}$), 7.27 (s, 2H, merged with $CDCl_3$ peak, C*H*$_{olefinic}$), 7.12 (s, 2H, *CH*), 1.03 (s, 18H, C(*CH*$_3$)$_3$), 1.44−1.03 (m, B*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6−174.4 (bm, NCN), 134.6 (s, C_{arom}), 134.1 (s, C_{arom}), 133.0 (s, C_{arom}), 128.8 (s, C_{arom}), 128.5 (s, C_{arom}), 126.7 (s, C_{arom}), 125.8 (s, C_{arom}), 125.3 (s, C_{arom}), 124.2 (s, C_{arom}), 118.4 (s, $C_{olefinic}$), 63.1 (s, *CH*), 37.6 (s, *C*(CH$_3$)$_3$), 28.4 (s, C(*C*H$_3$)$_3$); ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ −32.89; IR (ν, cm^{-1}) 3742, 2955, 2149, 1485, 1251, 732; HRMS (ESI, m/z) calcd for $C_{33}H_{37}N_2$ ([M − BH$_2$]$^+$) 461.2951, found 461.2960.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra of molecules **3** and **5**−**8**, ^{11}B NMR spectra of complexes **5**−**8**, and CIF files giving X-ray crystal structures are available free of charge via the Internet at http://pubs.acs.org.

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