Borylated N-heterocyclic carbenes: rearrangement and chemical trapping

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Abstract: This study details attempts to access N-heterocyclic carbenes (NHCs) featuring the diazaborolyl group, {(HCNDipp)$_2$B}, as one or both of the N-bound substituents, in order to generate strongly electron-donating and sterically imposing new carbene ligands. Attempts to isolate N-heterocyclic carbenes based around imidazolylidene or related heterocycles, are characterized by facile N-to-C migration of the boryl substituent. In the cases of imidazolium precursors bearing one N-bound diazaborolyl group and one methyl substituent, deprotonation leads to the generation of the target carbenes, which can be characterized *in situ* by NMR measurements, and trapped by reactions with metal fragments and elemental selenium. The half-lives of the free carbenes at room temperature range from 4-50 h (depending on the pattern of ancillary substituents) with N-to-C2 migration of the boryl function being shown to be the predominant rearrangement pathway. Kinetic studies show this to be a first order process that occurs with an entropy of activation close to zero. DFT calculations imply that an intramolecular 1,2-shift is mechanistically feasible, with calculated activation energies of the order of 90-100 kJ mol^{-1} reflecting the retention of significant aromatic character in the imidazole ring in the transition state. Trapping of the carbene allows for evaluation of steric and electronic properties via systems of the type LAuCl, LRh(CO)$_2$Cl and LSe. A highly unsymmetrical (but nonetheless bulky) steric profile and moderately enhanced σ-donor capabilities (compared to IMes) are revealed.

Introduction

Singlet carbenes have attracted a huge amount of interest in the past three decades, following initial reports from Bertrand and Arduengo.[1,2] This reflects not only their application as ancillary ligands in a range of Noble metal catalysts (drawing on the strength of the associated M–C bonds),[3] but also their use as bespoke donors for the stabilization of a range of compounds featuring *p*-, *d*- and *f*-block metals with unprecedented structural motifs.[4] CR$_2$ species of this type feature a filled σ-type orbital as the HOMO, with a formally vacant pπ-orbital typically being the LUMO.[4] The HOMO-LUMO energy gap is critical in dictating patterns of reactivity and donor properties as ligands, and can be tuned, for example by variation in the R substituents or by adjusting the angle at carbon. The most common class of carbenes, N-heterocyclic carbenes (NHCs), feature α-nitrogen substituents that are both σ-withdrawing and π-donating. These features, together with the incorporation of the carbene into a cyclic structure, serve to increase the HOMO-LUMO gap and thus stabilize the NHC. In addition, sterically demanding N-substituents provide kinetic stabilization with respect to dimerization.[2]

We have recently been interested in employing the bulky Dipp-substituted diazaborolyl group {(HCDippN)$_2$B} (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) as an strongly donating ancillary ligand, in order to synthesize highly electron-rich metal complexes.[5-7] The sensitivity of the nucleophilic lithium reagent {(HCDippN)$_2$B}Li(THF)$_2$,[5] however, prompted us to examine routes for incorporating the boryl group not as a directly bound ligand, but as a modulating substituent within, for example, an amido or alkoxo framework. Thus, for example, we recently reported the synthesis of the acyclic diamidosilylene, ({(HCDippN)$_2$B}(Me$_3$Si)N)$_2$Si, featuring a mixed boryl/silyl stabilized amide donor and which has an unusually wide angle at the silicon centre.[8] With this in mind, we were interested to examine the possible use of this particular boryl group as the N-bound substituent(s) within an NHC donor framework, hypothesizing that it would influence both the electronic and steric properties of the resulting carbene. Notably, strong σ-donation from the boryl substituents would be expected to augment the σ-donor capability of the carbene, and the presence of two bulky boryl N-substituents would likely generate very high peripheral steric loading. Examples of carbenes featuring boryl groups as α-substituent(s), or positioned more remotely, are not common, and to our knowledge there are no examples of isolable NHCs featuring an exocyclic N-boryl group.[9]

Results and Discussion

Syntheses of imidazolium and related precursors

Synthetically, N-borylated systems featuring an imidazolylidene or the corresponding benzannulated core appeared to present viable synthetic targets. With this in mind, we set about synthesizing the precursor imidazolium salts via reactions of the readily available bromoborane {(HCDippN)$_2$}BBr[5a,10] with the parent heterocycles (Scheme 1). In both cases, the introduction of the first boryl function could be achieved readily via the reactions of imidazole/benzamidazole, bromoborane and a potent base such as K[N(SiMe$_3$)$_2$]. Both monoborylated heterocycles **1** and **2** could be characterized by standard spectro

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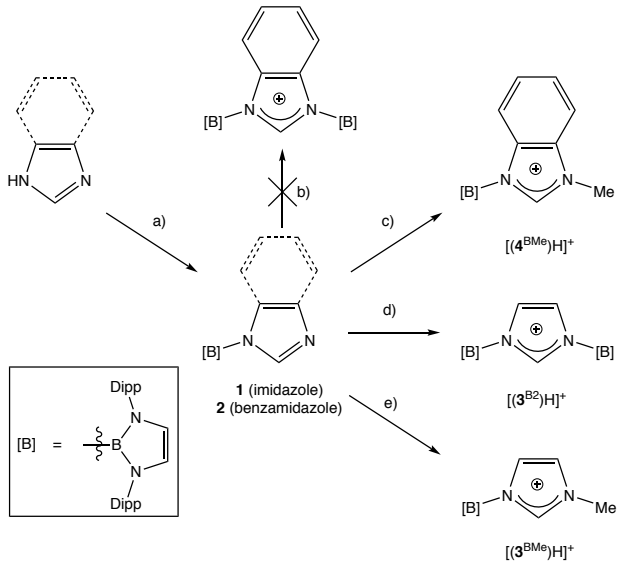


Scheme 1. Syntheses of borylated imidazolium salts from the bromoborane {(HCDippN)$_2$}BBr (counter-ions omitted for clarity). Reagents and conditions: (a) {(HCDippN)$_2$}BBr (1.0 equiv.), ^{n}BuLi (1.5 equiv.), Et$_2$O, -78^{o}C to RT, 80-90% *or* {(HCDippN)$_2$}BBr (1.0 equiv.), K[N(SiMe$_3$)$_2$] (1.0 equiv.), benzene, RT, 15 min.,40-50%; (b) excess {(HCDippN)$_2$}BBr, base, benzene or pyridine 115 ^{o}C; (c) MeOTf (1.1 equiv.), hexane, RT, 12 h ; (d) (from 1) {(HCDippN)$_2$}BBr (1.0 equiv.), Na[BPh$_4$] (1 equiv.), MeCN, 90%; (directly from imidazole) {(HCDippN)$_2$}BBr (2.7 equiv.), K[N(SiMe$_3$)$_2$] (1.0 equiv.), benzene, RT, 1 h, then removal of volatiles, Na[BPh$_4$], MeCN., 80-90%; (e) MeOTf (1.1 equiv.), hexane, RT, 4 h, 85%.

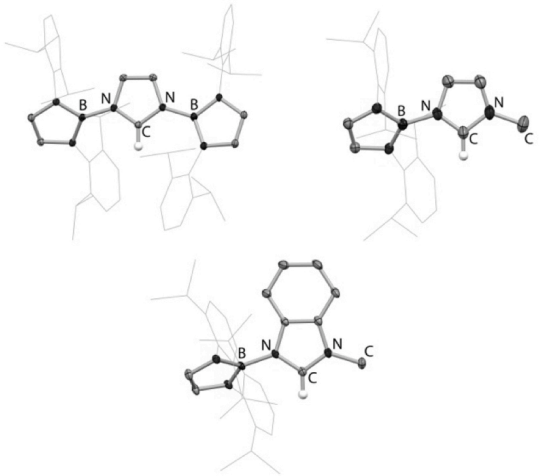


Figure 1. Molecular structures of [(**3**^{B2})H][BPh$_4$] (upper left), [(**3**^{BMe})H][OTf] (upper right) and [(**4**^{BMe})H][OTf] (lower), in the solid state as determined by X-ray crystallography. Counter-ions and most hydrogen atoms omitted, and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 35% probability level. Structural data for **1** and **2** are included in the ESI.

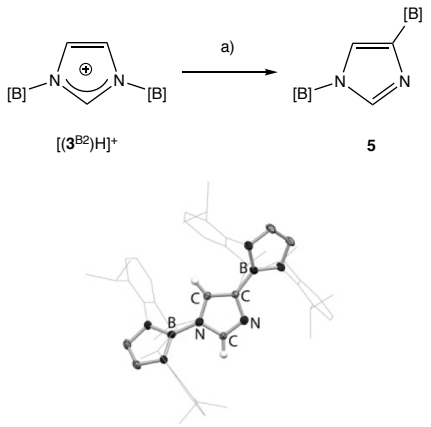
-scopic/analytical techniques, and their structures in the solid state confirmed by X-ray crystallography (see ESI). The introduction of a second boryl substituent proves to be more challenging, and in the case of the less basic (and more sterically hindered) benzimidazole system **2** we were unable to effect borylation of the remaining heterocycle nitrogen. On the other hand, imidazole **1** reacts with {(HCDippN)$_2$}BBr in aceto-nitrile solution to give the target bis(boryl)imidazolium cation [(**3**^{B2})H]$^+$ in good yield (>80%) after anion metathesis using Na[BPh$_4$] (Scheme 1). Exchange of bromide for a more weakly coordinating counter-ion is found to be critical to the stability of [(**3**^{B2})H]$^+$; the bromide salt – although stable in polar solvents – spontaneously undergoes the reverse reaction to regenerate bromoborane and **1** in non-polar media such as benzene. By contrast, [(**3**^{B2})H][BPh$_4$] is perfectly stable and can be re-crystallized from dichloromethane/hexane, and characterized both by standard spectroscopic/analytical techniques and by X-ray crystallography (Scheme 1 and Figure 1).

More active electrophiles such as MeOTf react with both **1** and **2** to give the corresponding unsymmetrical imidazolium/benz-imidazolium cations [(**3**^{BMe})H]$^+$ and [(**4**^{BMe})H]$^+$. These systems are very conveniently prepared as the respective triflate salts, by the addition of MeOTf to **1** or **2** in hexane. The product in each case precipitates out of solution as an analytically pure material. Single crystals of both compounds could be obtained from acetonitrile solution, with the structural data obtained from X-ray crystallography revealing comparable B–N distances [1.491(3)-1.499(7) Å] and N–C–N angles [106.9(6) and 110.6(2)-111.4(2)^o] to those measured for [(**3**^{B2})H][BPh$_4$] [1.496(4) and 1.499(4) Å; 110.2(2)^o].

Deprotonation chemistry

Attempts to deprotonate these imidazolium salts using alkyl or aryllithiums lead to nucleophilic attack either at C2, or at one of the boron centres (see ESI), so attention was turned instead to bulky amide bases. In the case of [(**3**^{B2})H][BPh$_4$], reaction with Na[N(SiMe$_3$)$_2$] or K[N(SiMe$_3$)$_2$] does indeed lead to deprotonation (as determined by mass spectrometry and microanalysis), but examination of the product by ^{1}H NMR spectroscopy reveals a lower symmetry product than would be expected for deprotonation at C2 (e.g. two boryl heterocycle CH signals at δ_H = 6.06 and 6.14 ppm). X-ray crystallography reveals that the product **5** in fact results from deprotonation at the backbone C4 position with an accompanying N-to-C migration of the boryl function (Scheme 2). The thermodynamic driving force for such a rearrangement can readily be understood in terms of the generation of a two-coordinate imidazole nitrogen (rather than a carbenic carbon) with migration of the boryl group to C4 (rather than, for example, to C2) being understood on steric grounds. Consistently, DFT studies of the relative energies of various isomeric forms of **5** show that the observed product is significantly more stable than the C2-borylated or carbenic isomers (Figure 2).

With this in mind, attempts were made to prevent boryl migration to the C4 position by blocking the backbone sites with methyl groups. The corresponding 4,5-dimethylimidazolium system, [(**6**^{B2})H][BPh$_4$] was synthesized in similar fashion to [(**3**^{B2})H][BPh$_4$] (Scheme 3; see ESI for structural character-ization) and its chemistry towards K[N(SiMe$_3$)$_2$] investigated. However, here too, deprotonation does not appear to take place at the C2 position. The product (**7**) has been characterized by NMR and mass spectrometry and, judged by the presence of



Scheme 2. (upper) Backbone deprotonation of [(**3**^{B2})H][BPh_4] with accompanying boryl group migration to yield **5** (counter-ions omitted for clarity). Reagents and conditions: (a) NMR scale: Na[$N(SiMe_3)_2$] (1.1 equiv.), C_6D_6, RT, quantitative by ^{1}H NMR; preparative scale uses K[$N(SiMe_3)_2$] giving 55% yield (ca. 1 g). (lower) Molecular structure of **5** in the solid state as determined by X-ray crystallography; most hydrogen atoms omitted and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 35% probability level.

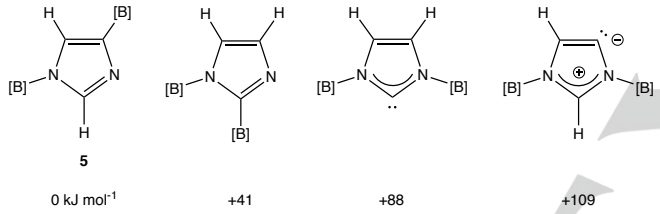
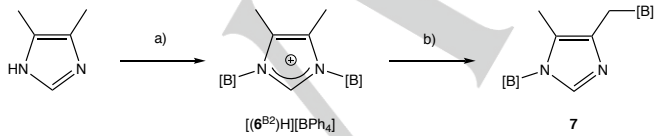


Figure 2. Relative energies (*E*, kJ mol^{-1}) of isomeric forms of **5**.

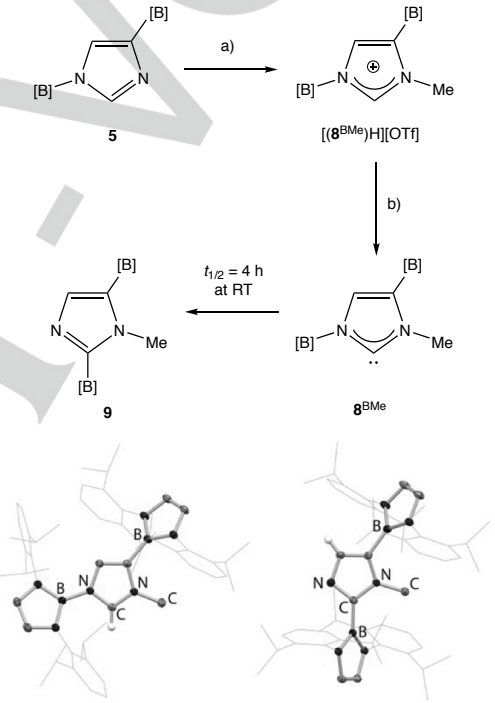
two distinct sets of boryl substituent resonances, does not retain the plane of symmetry present in [(**6**^{B2})H]$^+$. The ^{1}H NMR spectrum also contains only one backbone methyl signal (at δ_H = 1.40 ppm) integrating to three protons, and features a second signal at δ_H = 2.06 ppm integrating to 2H; the proton bound to C2 is also retained. Although **7** could not be isolated as single crystals suitable for X-ray crystallography, we propose on the basis of its spectroscopic signature that its formation involves deprotonation of one of the two backbone methyl substituents with accompanying N-to-C boryl group migration (Scheme 3).



Scheme 3. Generation and deprotonation of [(**6**^{B2})H][BPh_4] with accompanying boryl group migration to yield **7** (counter-ions omitted for clarity). Reagents and conditions: (a) {(HCDippN)$_2$}BBr (2.0 equiv.), K[$N(SiMe_3)_2$] (1.0 equiv.), benzene, RT, 1 h, then Na[BPh_4] (1.0 equiv.), MeCN, RT, 15 min, 31%; (b) K[$N(SiMe_3)_2$] (1.0 equiv.), benzene, RT, 2 h, 30%. Structural data for [(**6**^{B2})H][BPh_4] are included in the ESI.

C2 carbene generation and rearrangement

Given the fact that the rearranged system **5** features a pendant imidazole function, we hypothesized that alkylation at nitrogen might be possible to generate an unsymmetrical imidazolium cation analogous to [(**4**^{BMe})H]$^+$ and [(**3**^{BMe})H]$^+$. In such a case (Scheme 4), the propensity of the remaining N-boryl function to migrate to the backbone carbon would presumably be reduced on steric grounds. Accordingly, methylation of **5** with methyl triflate was examined, and the N-boryl-N'-methyl imidazolium salt [(**8**^{BMe})H][OTf] shown to be accessible in good (70-80%) yield. Moreover, in contrast to both [(**3**^{B2})H][BPh_4] and [(**6**^{B2})H][BPh_4], deprotonation of [(**8**^{BMe})H][OTf] leads to the formation of a carbene via deprotonation at C2 (Scheme 4).



Scheme 4. (upper) Deprotonation of [(**8**^{BMe})H][OTf] to yield the persistent carbene **8**^{BMe} and ultimately C2-borylated **9** (counter-ions omitted for clarity). Reagents and conditions: (a) MeOTf (1.0 equiv.), benzene, 3 h, 76%; (b) (carried out in situ) K[$N(SiMe_3)_2$] (1.0 equiv.), toluene-d_8, -78^{o}C, 1 h. (lower) Molecular structures of [(**8**^{B2})H][OTf] (left) and **9** (right) in the solid state as determined by X-ray crystallography. Counter-ions and most hydrogen atoms omitted, and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 35% probability level.

Thus, the reaction of [(**8**^{BMe})H][OTf] with K[$N(SiMe_3)_2$] in toluene leads to the clean generation of **8**^{BMe} which has been characterized by *in situ* NMR measurements and trapped via reactions with metal reagents as the corresponding NHC complex (*vide infra*). Spectroscopically, deprotonation is characterized by the disappearance of the ^{1}H NMR resonance at δ_H = 8.57 ppm assigned to the imidazolium C2 proton of [(**8**^{BMe})H][OTf], and the appearance of a new ^{13}C signal at δ_C = 225.8 ppm characteristic of a carbene centre (cf. 220.6 ppm for

IMes).[11] Although **8**^{BMe} can be obtained cleanly *in situ* at room temperature, it undergoes rearrangement with a half-life of ca. 4 h to give a second species which features no ^{13}C NMR signals at lower field than δ_C = 150 ppm. This compound can be shown by single crystal X-ray diffraction to be the N-to-C2 boryl migration product **9** (Scheme 4).

While intramolecular 1,2-shifts in singlet carbenes are well studied,[12–14] such rearrangements in imidazolylidenes have generally been considered kinetically unfavourable. This is due to the dearomatization of the five membered heterocycle required in the transition state in order to accommodate transfer of the electron pair associated with the migrating R group to the carbene pπ-orbital.[15] *Inter*molecular pathways have been demonstrated by crossover experiments both by Bertrand *et al.*[14] and by Chiu *et al.*[9e] In the former case – involving the N-to-C shift of a silyl substituent – migration involves nucleophilic attack by the carbene centre of one molecule on the silyl group of another. The rate-determining step is expected to be bimolecular and would be expected to be accompanied by a significant negative entropy of activation. By contrast, in the case of the N-borylated system examined by Chiu and co-workers, a radical pathway is favoured.[9e,16] The rate-determining step is presumably the (unimolecular) homolytic cleavage of the N–B bond, implying a large positive entropy of activation. With this in mind, we sought to obtain kinetic data on the rearrangement of **8**^{BMe} to **9**, with the aim of differentiating between different possible mechanistic pathways.

Monitoring by *in situ* ^{1}H NMR spectroscopy was carried out at temperatures in the range 298-323 K, with the behaviour of the resonances due to **8**^{BMe} as a function of time being found to be consistent with first order kinetics (Figure 3). The data obtained at 298 K yield a rate constant, k = (4.80 ± 0.04) x 10^{-5} s^{-1}, which implies a half-life at that temperature of 4.01 ± 0.07 h. These analyses suggest that the rate-determining step in this particular rearrangement is unlikely to involve two molcules of **8**^{BMe}.[14]

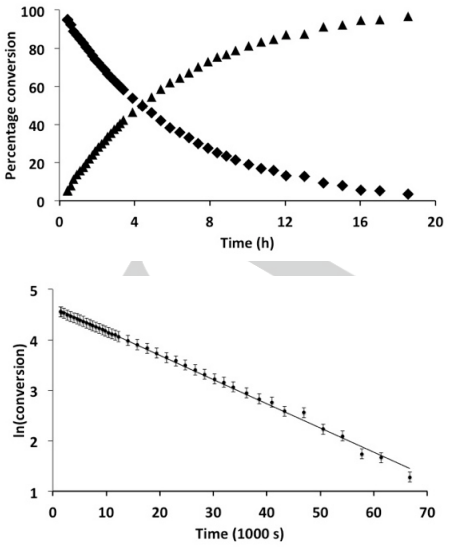


Figure 3. Rearrangement of **8**^{BMe} (◆) to **9** (▲) at 298 K in toluene-d_8 solution, as determined by the behaviour of ^{1}H NMR resonances of the two species.

Determination of the rate constant as a function of temperature allows for estimation of the enthalpy and entropy of activation using a conventional Eyring plot (Figure 4; $\Delta H^{‡}$ = 97 ± 2 kJ mol^{-1} and $\Delta S^{‡}$ = -3.1 ± 0.2 J mol^{-1} K^{-1}, respectively). Interestingly, while these data imply a relatively large enthalpy of activation – consistent with a significant degree of bond breakage in the rate-determining transition state, the *entropy* of activation is very close to zero. This is difficult to reconcile on the basis of the expectations for either an intermolecular nucleophilic or dissociative radical pathway. As a further probe of the latter pathway, experiments were carried out involving either EPR monitoring or the use of radical traps (TEMPO, 2,3-dimethylbutadiene), but in neither case was any evidence obtained for the formation of any radical intermediates.

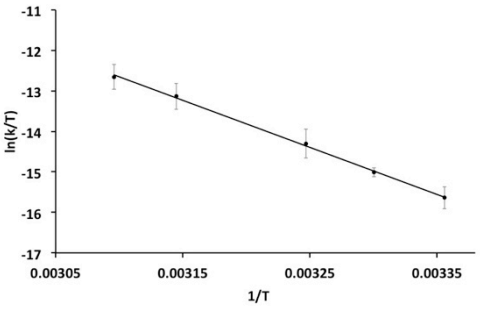


Figure 4. Eyring plot based on rate constants derived at temperatures in the range 298-323 K for the rearrangement of **8**^{BMe} to **9**.

As noted previously, the barriers associated with direct intramolecular 1,2-shifts in aromatic NHCs have been calculated to be too high to be mechanistically compatible with the observed reactivity.[15,17] In part, this is thought to reflect the need for de-aromatization to allow for interaction of the exocyclic σ-bond of the migrating group and the empty pπ-orbital of the carbene. Given the very small magnitude of $\Delta S^{‡}$ measured for the rearrangement of **8**^{BMe}, however, we wondered whether such a mechanism might be feasible in this case. With this in mind, we carried out DFT calculations on a model system in which the ^{i}Pr groups of the Dipp substituents were replaced by methyl groups for computational efficiency. A transition state could be located corresponding to intramolecular N-to-C migration of the boryl group (Figure 5) with a free energy of activation of $\Delta G^{‡}$ = 92 kJ mol^{-1} (at 298 K). This activation barrier is not only similar to the experimentally determined value at the same temperature ($\Delta G^{‡}_{298}$ = 98 ± 2 kJ mol^{-1}), but is significantly lower than the values calculated for other N-heterocyclic systems, *e.g.* 288 kJ mol^{-1} for the 1,2-shift of hydrogen in 2,3-dihydroimidazol-2-ylidene,[17] and 177 kJ mol^{-1} for the 1,2-shift of hydrogen in 2,3-dihydrothiazol-2-ylidene.[18] Further evidence that the calculated transition state in the case of **8**^{BMe} might have some experimental validity comes from the fact that the enthalpy and entropy of activation derived from the DFT studies ($\Delta H^{‡}$ = 95 kJ mol^{-1}, $\Delta S^{‡}$ = 9 J mol^{-1} K^{-1}) are similar to the experimental values (97 ± 2 kJ mol^{-1}, $\Delta S^{‡}$ = -3.1 ± 0.2 J mol^{-1} K^{-1}).

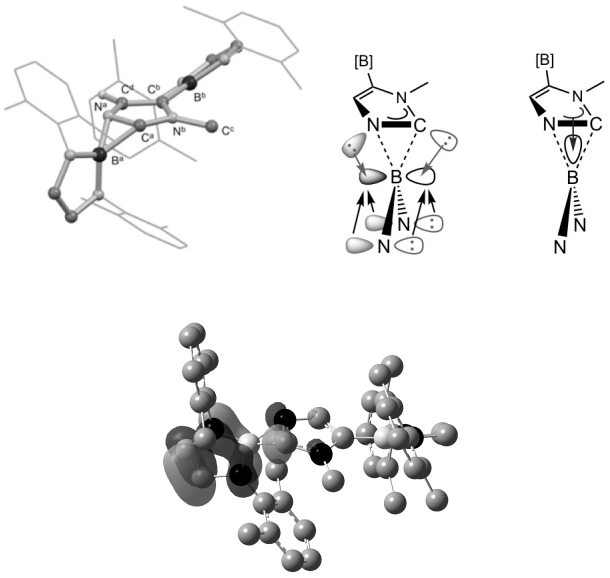


Figure 5. (upper left) Structure obtained by DFT methods for the transition state in the 1,2-shift of the boryl group in a model of $\mathbf{8}^{BMe}$ (in which Dipp groups have been replaced by Xylyl). Most hydrogen atoms omitted and Xyl groups shown in wireframe format for clarity. (upper right) Schematic of the electronic stabilization of the electrophilic boron centre in the transition state. (lower) DFT-calculated HOMO for the transition state showing interactions between N- and C- atoms and the boryl heterocycle π system (isovalue = 0.05).

The structure of the transition state is depicted in Figure 5, and shows that the boron centre of the migrating boryl group is almost equidistant between the nitrogen and carbon atoms (1.598, 1.698 Å). The resulting BNC plane is orientated at an angle of ca. 37° to that of the imidazole unit, and the pendant boryl heterocycle lies approximately perpendicular to the imidazole plane. Comparison of the geometry of the imidazole ring in the transition state with that determined experimentally for the analogous unit in imidazolium salt [($\mathbf{8}^{BMe}$)H][OTf] reveals close similarities. Both heterocycles are planar and the N–C–N angle [109.0 vs 109.7(1)°] and C–N distances relating to the carbenic carbon are very similar [1.351/1.350 vs 1.344(2)/1.320(2) Å]. As such, the geometry calculated for the heterocycle in the transition state implies little loss of aromaticity.

With this in mind, we postulate that the migration of the boryl group draws on its electrophilic character at boron, allowing it to 'shuttle' between the exocyclic N- and C2-centred lone pairs, and as such, effect a 1,2-shift without significant dearomatization of the imidazole heterocycle (Figure 5). The orientation of the boryl group allows for interaction of the vacant pπ-orbital at boron with the σ-orbitals (lone pairs) of both nitrogen and the carbene carbon. While these interactions might be expected to be optimized by keeping the migrating boron centre in the imidazole plane, positioning it below the plane (Figure 5) allows for additional stabilization of the electron deficient boron centre via donation from the imidazole π-system into the boron σ-orbital.

With this 1,2-rearrangement in mind, we next sought to examine the deprotonation chemistry of the closely related system [($\mathbf{3}^{BMe}$)H][OTf] (Scheme 1). The reaction with K[N(SiMe$_3$)$_2$] in toluene proceeds along similar lines to that with [($\mathbf{8}^{BMe}$)H][OTf], leading to the generation of a transient free carbene which rearranges via N-to-C2 migration of the boryl substituent. The carbene in this case is characterized by a ^{13}C signal at δ_C = 223.6 ppm, and (as judged by in situ ^{1}H NMR monitoring) is significantly longer lived than $\mathbf{8}^{BMe}$ (Figure 6). Thus, the half-life determined experimentally for $\mathbf{3}^{BMe}$ at 298 K (49 ± 1 h) is an order of magnitude longer than that measured for $\mathbf{8}^{BMe}$. A transition state corresponding to intra-molecular N-to-C boryl migration could also determined computationally for $\mathbf{3}^{BMe}$; this has similar structure features to that calculated in the case of $\mathbf{8}^{Me}$, and is associated with an activation energy ($\Delta G^{\ddagger}$ = 99 kJ mol^{-1}) which is marginally higher than that calculated for $\mathbf{8}^{BMe}$ (92 kJ mol^{-1}). This finding is not only consistent with experiment, but also with the notion that the electrophilic boron centre in the transition state should be stabilized to a greater degree by the more electron-rich (backbone borylated) imidazole heterocycle found in $\mathbf{8}^{BMe}$.

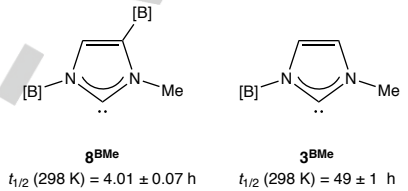
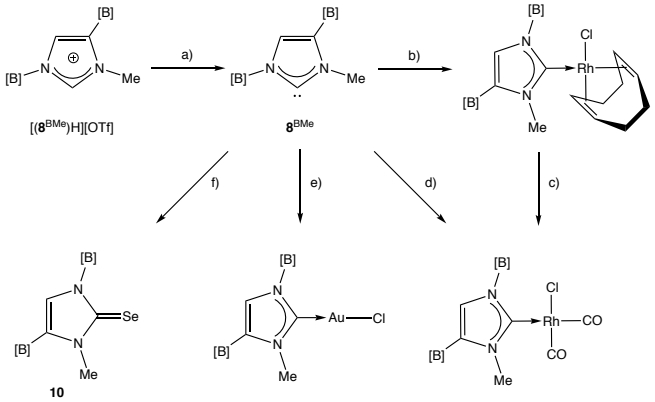


Figure 6. Half-lives determined for boryl-substituted NHCs based on in situ NMR studies.

Carbene trapping

While $\mathbf{8}^{BMe}$ could not be structurally characterized by X-ray crystallography, comparison with related systems *could* be accomplished through the synthesis of transition metal and main group derivatives of types that have previously been used to gauge the steric and electronic properties of NHCs. The percentage buried volume (%V_{bur}) of a carbene ligand is often calculated from the respective AuCl complex,[19] and with like-for-like comparison of the steric properties of $\mathbf{8}^{BMe}$ in mind, its coordination to the AuCl fragment was investigated. Accordingly, ($\mathbf{8}^{BMe}$)AuCl was synthesized from the *in situ* generated carbene and (THT)AuCl, and isolated in 34% yield (Scheme 5). A singlet at 177.0 ppm is observed in the ^{13}C NMR spectrum, consistent with other gold carbene complexes,[20] and ($\mathbf{8}^{BMe}$)AuCl could additionally be characterized by X-ray crystallography (Figure 7). The expected linear coordination geometry at gold is confirmed [178.0(1)°], with a decidedly unsymmetrical steric profile being presented at the metal by the N-bound boryl and methyl groups of the $\mathbf{8}^{BMe}$ carbene (see Figure 8 for topographic map obtained using the SambVca 2.0 program).[19f] The percentage buried volume (%V_{bur}) could be calculated from the solid state structure of ($\mathbf{8}^{BMe}$)AuCl (50.0%), which despite the presence of one N-methyl group, places $\mathbf{8}^{BMe}$ among the bulkier carbenes reported to date (cf. IDipp 44.5%, 6Dipp 50.8%, 7Dipp 52.6%).[19e,21]



Scheme 5. Formation of metal/selenium derivatives from borylated NHC **8**^{BMe}. Reagents and conditions: (a) K(N(SMe$_3$)$_2$] (1.0 equiv., benzene, RT, 5 min, used *in situ*; (b) [Rh(cod)Cl]$_2$ (0.5 mmol of dimer), benzene, RT, 30 min, 40%; (c) CO (1 atm.), quantitative by NMR; (d) [Rh(CO)$_2$Cl]$_2$ (0.45 mmol of dimer), benzene, 10 min, quantitative by NMR; (e) (THT)AuCl (1.0 equiv.), toluene, -40°C to RT, 30 min, 34%; (f) Se powder (ca. 4 equiv.), benzene, RT, 1 h, 66%.

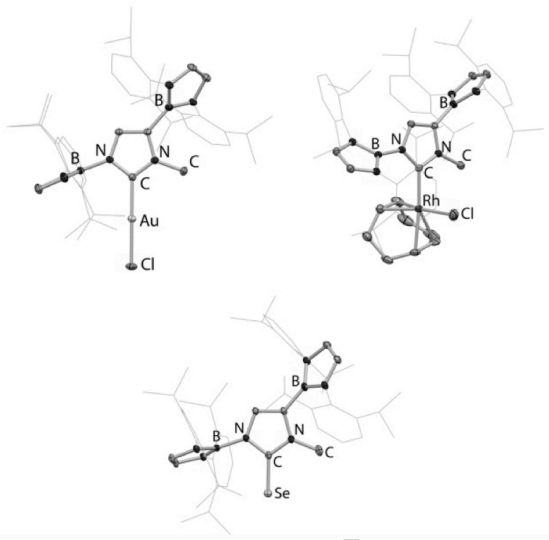


Figure 7. Molecular structures of (**8**^{BMe})AuCl (upper left), (**8**^{BMe})Rh(cod)Cl (upper right) and **10** (lower) in the solid state as determined by X-ray crystallography. Minor disorder component and most hydrogen atoms omitted and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 35% probability level. The structure of *cis*-(**8**^{BMe})Rh(CO)$_2$Cl is included in the ESI.

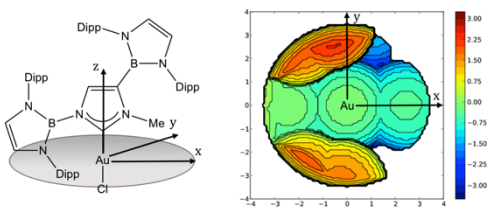


Figure 8. Topographic steric map of (**10**^{BMe})AuCl complex.[19f]

The electronic properties of **8**^{BMe} were also probed, making use of the [Rh(CO)$_2$Cl] complex to allow for calculation of the Tolman Electronic Parameter (TEP).[22] (**8**^{BMe})Rh(CO)$_2$Cl could be synthesized via two routes, either directly from [Rh(CO)$_2$(μ-Cl)]$_2$ or through the intermediacy of (**8**^{BMe})Rh(cod)Cl.[23] In the latter case, the cyclooctadiene complex was first synthesized by reacting *in situ* generated **8**^{BMe} with [Rh(cod)Cl]$_2$ and isolated in 40% yield. Spectroscopically, its formation is signalled by appearance of a doublet in the ^{13}C NMR spectrum at 189.0 ppm ($^1J_{RhC}$ = 52.0 Hz), and confirmed by X-ray crystallography (Figure 7). Reaction with CO in C_6D_6 then allows access to the dicarbonyl complex (**8**^{BMe})Rh(CO)$_2$Cl.[23] Single crystals of the latter could be obtained, allowing for crystallographic proof of composition, although the diffraction data was not of sufficiently high quality to allow for discussion of structural metrics (see ESI). The mutually *cis* disposition of the two carbonyl ligands is consistent with the ^{13}C NMR spectrum, which contains three doublets in the range 180-190 ppm due to inequivalent carbonyl groups and the carbene carbon.

The two CO stretching bands can be found at 1990 and 2069 cm^{-1}, based on solution-phase samples of *cis*-(**8**^{BMe})Rh(CO)$_2$Cl in dichloromethane. The average CO stretching frequency so obtained (2030 cm^{-1}) then allows for the determination of a value of 2043 cm^{-1} for the TEP.[24] This value is lower than that for IMes (2051 cm^{-1}),[24] suggesting increased electron density at the metal centre, and is similar to those determined for SIMes (2048 cm^{-1}) and 6Mes (2042 cm^{-1}).[25] Superficially, this implies that **8**^{BMe} is a better σ-donor than IMes, and comparable to SIMes/6Mes. It needs to be borne in mind, however, that saturated NHCs typically also have enhanced π-acidity compared with imidazolylidene-derived systems,[26,27] which reduces the overall electron density at the metal and thus increases the value of the TEP. To allow for systematic comparison between ligands, independent estimation of the π-acidity of **8**^{BMe} was carried out.

Selenium adducts of carbenes offer a useful probe for estimating their π-acidity and **10** was therefore synthesized from *in situ* generated **8**^{BMe} and selenium powder, and isolated in 66% yield (Scheme 5). Single crystals of the compound **10** suitable for X-ray crystallography could be obtained by recrystallization from benzene (Figure 7); the ^{77}Se NMR spectrum of crystalline samples redissolved in acetone-d$_6$ show a signal at δ_{Se} = 67 ppm. This shift is significantly lower than those of the saturated NHCs SIMes (δ_{Se} = 181 ppm) and 6Mes (δ_{Se} = 271 ppm),[26] and similar to that of IMes (δ_{Se} = 87 ppm), implying (i) that **8**^{BMe} is markedly less π-accepting than saturated NHCs; and (ii) that (by comparison with IMes) π-acidity is not greatly affected by the presence of the N-bound boryl group.

The π-acidity of **8**^{BMe} is similar to IMes and so comparison of the two TEP values implies that the presence of the boryl groups in the former augments its σ-donor abilities. On the other hand, the π-acidity of **8**^{BMe} is lower than that of (for example) 6Mes, and the fact that the TEP values of the two systems are very similar, indicates that the σ-donor properties of **8**^{BMe} are somewhat lower than 6Mes. As such, σ-donor capabilities intermediate between IMes and 6Mes are indicated. This conclusion is further supported by the results of DFT

calculations on the three ligands, which imply that the HOMO energies for the free carbenes fall in the order -421 kJ mol^{-1} (6Mes) > -441 kJ mol^{-1} (**8**^{BMe}) > -475 kJ mol^{-1} (IMes).[28]

Conclusions

We have attempted to access N-heterocyclic carbenes (NHCs) featuring the diazaborolyl group, {(HCNDipp)$_2$B}, as one or both of the N-bound substituents, in order to generate strongly electron-donating and sterically imposing new carbene ligands. However, attempts to isolate N-borylated imidazolylidenes featuring this particular group are frustrated by very ready N-to-C migration of the boryl substituent. In the cases of imidazolium precursors bearing one N-bound diazaborolyl group and one methyl substituent, deprotonation leads to the generation of the target carbenes, which can be characterized by *in situ* NMR measurements, and trapped by reactions with metal fragments and elemental selenium. The half-lives of these free carbenes at room temperature vary by an order of magnitude (depending on ancillary substituents), with N-to-C2 migration of the boryl function being shown to be the predominant rearrangement pathway. Kinetic studies on **8**^{BMe} show this to be a first order process that occurs with an entropy of activation close to zero. DFT calculations imply that an intramolecular 1,2-shift is feasible, with calculated activation energies of the order of 90-100 kJ mol^{-1} reflecting the retention of significant aromatic character in the imidazole ring in the transition state. While such a pathway has previously been associated with much higher activation barriers for hydride or silyl group migration, the reasons underpinning this alternative pathway might arise from the fact that the migrating group possesses a vacant pπ-orbital, which allows for shuttling of the electrophilic boryl function between putative N and C lone pairs. That said, the BMes$_2$ group also possesses a vacant p$_\pi$-orbital and experimental data is consistent with an intermolecular (radical) pathway for the corresponding 1,2-carbene rearrangement.[9e] A significant difference between BMes$_2$ and the diazaborolyl moiety, however, is the presence of π-donating nitrogen atoms α to the boron centre in the latter, which potentially serve to stabilize the migrating (electrophilic) boryl fragment and thus lower the energy of the transition state for the direct 1,2-shift.

Experimental Section

General methods and instrumentation

All manipulations were carried out using standard Schlenk line and glove box techniques under an atmosphere of argon and dinitrogen, respectively. With the exceptions of tetrahydrofuran and diethyl ether, solvents were dried using a commercially available Braun SPS. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone. Imidazole was sublimed in vacuo at 120°C; benzimidazole and 4,5-diphenylimidazole were dried in vacuo at 100°C. Methyl trifluoromethanesulfonate, sodium bis(trimethylsilyl)amide, potassium bis(trimethylsilyl)amide and selenium powder were used as received. {(HCDippN)$_2$}BBr,[10] (THT)AuCl,[29] [Rh(cod)Cl]$_2$,[30] and [Rh(CO)$_2$Cl]$_2$[31] were synthesized according to literature procedures. ^{1}H, ^{13}C{^{1}H}, ^{11}B, ^{19}F and ^{77}Se NMR spectra were measured on a Bruker Avance III HD nanobay 400 MHz or a Bruker AVC500 spectrometer and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B and ^{19}F NMR spectra were referenced to external Et$_2$O·BF$_3$ and ^{77}Se NMR spectra to SePh$_2$ in CDCl$_3$. Assignments were confirmed using two dimensional ^{1}H-^{1}H, ^{13}C-^{1}H and ROESY NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University.

Syntheses of novel compounds

1: Method (a) To a solution containing imidazole (0.29 g, 4.26 mmol) and {(HCDippN)$_2$}BBr (2.00 g, 4.28 mmol) in diethyl ether (20 mL) at -78°C was added dropwise ^{n}BuLi (2.6 mL of a 2.5 M solution in hexane, 6.4 mmol), and the reaction mixture warmed to room temperature overnight. The resulting solution was filtered, concentrated and stored at -25°C, leading to the formation of colourless crystals of **1** (as the diethyl ether mono-solvate). Yield: 2.30 g, 89%. Slow evaporation of a hexane solution yielded colourless single crystals suitable for X-ray crystallography. Method (b) Imidazole (0.06 g, 0.86 mmol), potassium bis(trimethylsilyl)amide (0.17 g, 0.86 mmol) and {(HCDippN)$_2$}BBr (0.40 g, 0.86 mmol) were dissolved in benzene (10 mL) and the reaction mixture stirred for 15 min at room temperature. The solution was filtered and the solvent removed in vacuo; recrystallization from acetonitrile yielded the product as colourless crystals, which were isolated by filtration, washed with cold acetonitrile (3 x 3 mL) and dried in vacuo to yield **1** as a spectroscopically and analytically pure material. Yield: 0.16 g, 41%. ^{1}H NMR (MeCN-d$_3$, 400 MHz, 298 K): δ$_H$ 7.44-7.48 (m, 2H, p-H of Dipp), 7.34-7.36 (m, 4H, m-H of Dipp), 6.73 (m, NCHC<u>H</u>NB of imidazole), 6.64 (m, NC<u>H</u>CHNB of imidazole), 6.40 (s, 2H, N(CH)$_2$N of boryl group), 6.18 (m, 1H, NCHN), 3.00 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C<u>H</u>Me$_2$), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH<u>Me</u>$_2$), 0.98 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH<u>Me</u>$_2$). ^{13}C{^{1}H} NMR (MeCN-d$_3$, 101 MHz, 298 K): δ$_C$ 147.0 (o-C of Dipp), 139.8 (N<u>C</u>HCHNB of imidazole), 137.8 (ipso-C of Dipp), 129.9 (NCH<u>C</u>HNB of imidazole), 129.5 (p-C of Dipp), 125.1 (m-C of Dipp), 120.2 (NCHN), 119.9 (N(CH)$_2$N of boryl group), 66.2 (CH$_2$ of Et$_2$O solvate), 29.3 (<u>C</u>HMe$_2$), 24.6 (CH<u>Me</u>$_2$), 23.4 (CH<u>Me</u>$_2$), 15.6 (CH$_3$ of Et$_2$O solvate). ^{11}B NMR (C$_6$D$_6$, 128 MHz, 298 K): δ$_B$ 21 (br s, boryl ligand). MS(CI): m/z (assignment, %) 455.3 ([M]H$^+$, 6%). Acc. mass (EI): calc. for C$_{29}$H$_{40}$^{10}BN$_4$: 454.3382; meas.: 454.3383. Elemental microanalysis, meas. (calc. for C$_{29}$H$_{39}$BN$_4$): C 76.26 (76.64)%, H 8.76 (8.65)%, N 12.06 (12.33)%.

2: Benzimidazole (0.13 g, 1.07 mmol), {(HCDippN)$_2$}BBr (0.50 g, 1.07 mmol) and potassium bis(trimethylsilyl)amide (0.21 g, 1.07 mmol) were dissolved in benzene (15 mL) and the reaction mixture stirred for 1 h. The solution was filtered and the volatiles removed in vacuo. The crude product can be isolated at this point and used for subsequent steps without further purification (yield: 0.40 g, 74%). Alternatively, **2** can be purified by dissolving the crude compound in minimum acetonitrile at 80°C, and allowing the solution to cool slowly in the oil bath, to produce colourless crystals. These can be isolated by filtration, washed with acetonitrile (4 x 5 mL), and dried in vacuo to yield a spectroscopically and analytically pure product (0.22 g, 41%). Colourless single crystals suitable for X-ray crystallography were obtained from cold hexane. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ$_H$ 7.87 (1H, d, $^3J_{HH}$ = 7.8 Hz, benzimidazole o-H), 7.83 (1H, br s, NCHN), 7.14-7.18 (3H, overlapping m, p-H of Dipp and C$_6$D$_5$H), 7.04-7.06 (4H, m, m-H of Dipp), 6.96-6.99 (1H, m, benzimidazole m-H), 6.90-6.94 (2H, overlapping m, benzimidazole o-H and m-H), 6.23 (2H, s, N(CH)$_2$N of boryl ligand), 3.27 (4H, sept, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.14 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me</u>$_2$), 0.93 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me</u>$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 101 MHz, 298 K): δ$_C$ 145.7 (o-C of Dipp), 145.7 (N<u>C</u>CN), 145.0 (NCHN), 137.8 (i-C of

Dipp), 135.7 (NCCN), 128.6 (p-C of Dipp), 124.6 (m-C of Dipp), 122.9 (NCCH(CH)$_3$CN or NCCH(CH)$_2$CHCN), 122.8 (NCCH(CH)$_2$CHCN), 120.7 (NCCH(CH)$_3$CN), 119.7 (N(CH)$_2$N of boryl ligand), 113.0 (NCCH(CH)$_3$CN or NCCH(CH)$_2$CHCN), 28.9 (CHMe$_2$), 25.4 (CHMe$_2$), 23.0 (CHMe$_2$). ^{11}B NMR (C_6D_6, 128 MHz, 343 K): δ_B 22 (br s, boryl ligand). MS (EI): m/z (assignment, %) 504.3 ([M]$^+$, 14%). Acc. Mass EI: calc. for $C_{33}H_{41}{}^{10}BN_4$: 503.3455; found: 503.3405. Elemental microanalysis, found (calc. for $C_{33}H_{41}BN_4$): C 78.54 (78.56)%, H 8.59 (8.19)%, N 11.33 (11.11)%.

[(3^{B2})H][BPh$_4$]: Imidazole (0.08 g, 1.18 mmol), sodium bis(trimethylsilyl)amide (0.23 g, 1.18 mmol) and {(HCDippN)$_2$}BBr (1.50 g, 3.21 mmol) were dissolved in benzene (15 mL) and the reaction mixture stirred for 1 h. Volatiles were removed in vacuo and acetonitrile (15 mL) added; to the resulting solution was added Na[BPh$_4$] (0.42 g, 1.23 mmol) and the mixture stirred for 15 min. Volatiles were again removed in vacuo, and the resulting residue washed with benzene (3 x 10 mL) to yield [(3^{B2})H][BPh$_4$] as a pale brown powder. Yield: 1.20 g, 86%. Single crystals suitable for X-ray crystallography were obtained by layering a solution in dichloromethane with hexane. ^{1}H NMR (MeCN-d$_3$, 400 MHz, 298 K): δ_H 7.45-7.49 (4H, m, p-H of Dipp), 7.30-7.36 (8H, m, o-H of [BPh$_4$]$^-$), 7.28-7.30 (8H, m, m-H of Dipp), 7.01-7.04 (9H, overlapping m, m-H of [BPh$_4$]$^-$ and NCHN), 6.86-6.89 (4H, m, p-H of [BPh$_4$]$^-$), 6.62 (2H, br s, N(CH)$_2$N of imidazole), 6.43 (4H, s, N(CH)$_2$N of boryl ligand), 2.74 (8H, sept, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$), 1.15 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$), 0.85 (12H, d, $^3J_{HH}$ = 7.0 Hz, CHMe$_2$). ^{13}C{^{1}H} NMR (MeCN-d$_3$, 101 MHz, 298 K): δ_C 164.8 (q, $^1J_{CB}$ = 49.3 Hz, i-C of [BPh$_4$]$^-$), 145.7 (o-C of Dipp), 136.8 (br m, o-C of [BPh$_4$]$^-$), 136.1 (NCHN), 135.6 (i-C of Dipp), 130.5 (p-C of Dipp), 126.6 (br q, $^3J_{CB}$ = 2.7 Hz, m-C of [BPh$_4$]$^-$), 126.1 (m-C of Dipp), 125.9 (N(CH)$_2$N of imidazole), 122.7 (p-C of [BPh$_4$]$^-$), 121.5 (N(CH)$_2$N of boryl ligand), 29.5 (CHMe$_2$), 24.5 (CHMe$_2$), 23.8 (CHMe$_2$). ^{11}B NMR (MeCN-d$_3$, 128 MHz, 298 K): δ_B 19 (br s, boryl ligand), -7 (s, [BPh$_4$]$^-$). MS (ESI): m/z (assignment, %) 841.6 ([M]$^+$, 97%). Acc. Mass ESI: calc. for $C_{55}H_{75}B_2N_6$: 841.6251; found: 841.6246. Elemental microanalysis: found (calc. for $C_{79}H_{95}B_3N_6$): C 81.60 (81.72)%, H 8.36 (8.25)%, N 7.21 (7.24)%.

[(3^{BMe})H][OTf]: To a solution of **1** (0.01 g, 0.18 mmol) in hexane (3 mL) was added methyl trifluoromethanesulfonate (22 µL, 0.20 mmol) and the resulting mixture stirred for 4 h. The solution was filtered and the residue washed with hexane (3 x 2 mL) and dried in vacuo to yield the product as an off-white powder. Yield: 0.11 g, 85%. Colourless single crystals suitable for X-ray crystallography could be obtained by dissolving the product in a minimal amount of hexane at 60 °C and allowing the solution to cool slowly in the oil bath. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ_H 7.53 (1H, s, NCHN), 7.29 (2H, m, p-H of Dipp), 7.15-7.16 (5H, overlapping m, m-H of Dipp, NCHCHN of imidazole and C_6D_5H), 6.30 (1H, s, NCHCHN of imidazole), 5.95 (2H, s, N(CH)$_2$N of boryl ligand), 3.41 (3H, s, NMe), 2.93 (4H, sept, $^3J_{HH}$ = 6.8 Hz, CHMe$_2$), 1.08-1.11 (24H, overlapping d, CHMe$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 298 K): δ_C 145.8 (o-C of Dipp), 137.0 (NCHN), 135.5 (i-C of Dipp), 130.0 (p-C of Dipp), 126.2 (NCHCHN of imidazole), 125.2 (m-C of Dipp), 121.4 (NCHCHN of imidazole), 120.0 (N(CH)$_2$N of boryl ligand), 36.7 (NMe), 28.9 (CHMe$_2$), 24.8 (CHMe$_2$), 23.4 (CHMe$_2$). ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 19 (br s, boryl ligand). ^{19}F NMR (MeCN-d$_3$, 470 MHz, 298 K): δ_F -63.3. MS (EI): m/z (assignment, %) 469.4 ([M]$^+$, 99%). Acc. Mass EI: calc. for $C_{29}H_{40}{}^{10}BN_4$: 469.3502; found: 469.3607.

[(4^{BMe})H][OTf]: To a solution of **2** (0.17 g, 0.33 mmol) in hexane (5 mL) was added methyl trifluoromethanesulfonate (41 µL, 0.37 mmol) and the resulting mixture stirred overnight. After filtration, the residue was washed with hexane (2 x 3 mL) and dried in vacuo to yield the product as an off-white powder. Yield: 0.19 g, 87%. Colourless single crystals suitable for X-ray crystallography could be grown by dissolving the product in a minimal amount of acetonitrile at 80 °C and allowing the solution to cool slowly in the oil bath. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ_H 9.34 (1H, s, NCHN), 7.03-7.08 (4H, overlapping m, NCCH and p-H of Dipp), 6.99-7.00 (4H, m, m-H of Dipp), 6.86-6.89 (1H, ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.1 Hz, [B]NCCHCH), 6.81-6.84 (1H, ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, MeNCCHCH), 6.25 (2H, s, N(CH)$_2$N of boryl ligand), 3.58 (3H, s, NMe), 3.20 (4H, sept, $^3J_{HH}$ = 6.8 Hz, CHMe$_2$), 1.19 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$), 1.17 (12H, d, $^3J_{HH}$ = 6.8 Hz, CHMe$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K): δ_C 145.9 (o-C of Dipp), 144.7 (NCHN), 135.4 (i-C of Dipp), 132.7 (MeNCCH), 129.3 ([B]NCCH), 127.1 ([B]NCCHCH), 126.8 (MeNCCHCH), 124.7 (m-C of Dipp), 121.0 (N(CH)$_2$N of boryl ligand), 114.2 (MeNCCH), 114.0 ([B]NCCH), 33.8 (NMe), 29.1 (CHMe$_2$), 26.0 (CHMe$_2$), 23.5 (CHMe$_2$). ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 21 (br s, boryl ligand). ^{19}F NMR (C_6D_6, 377 MHz, 298 K): δ_F -77.7. MS (EI): m/z (assignment, %) 519.4 ([M]$^+$, 97%). Acc. Mass EI: calc. for $C_{34}H_{44}BN_2$: 519.3660; found: 519.3761. Elemental microanalysis: found (calc. for $C_{35}H_{44}BN_4F_3O_3S$): C 62.90 (62.87)%, H 6.54 (6.63)%, N 8.71 (8.38)%.

5: Method (a) (in situ): [(3^{B2})H][BPh$_4$] (0.01 g, 0.01 mmol) and sodium bis(trimethylsilyl)amide (ca. 0.002 g, 0.01 mmol) were dissolved in C_6D_6 (0.5 mL) in a J. Young's NMR tube. The solution turned dark brown immediately. The ^{1}H NMR spectrum measured after 10 min shows quantitative conversion to a single new product, **5**. Method (b) (preparative scale): Imidazole (0.15 g, 2.20 mmol), potassium bis(trimethylsilyl)amide (0.85 g, 4.26 mmol) and **1** (2.00 g, 4.28 mmol) were dissolved in pentane (40 mL) and stirred at room temperature. A white precipitate formed immediately and the solution stirred overnight. After filtration, the residual solid was extracted with pentane (2 x 5 mL) and the filtered extracts combined, concentrated and stored at -20 °C overnight producing colourless crystals. After filtration at -20 °C, the crystals were dried in vacuo to yield the product as a white crystalline solid. Yield 0.99 g, 55%. Colourless single crystals suitable for X-ray crystallography were obtained from diethyl ether at -20 °C. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ_H 7.16-7.19 (4H, overlapping m, p-H of C-boryl ligand and C_6D_5H), 7.09-7.13 (6H, overlapping m, m-H of C-boryl ligand and p-H of N-boryl ligand), 6.96-6.98 (4H, m, m-H of N-boryl ligand), 6.86 (1H, d, $^4J_{HH}$ = 0.8 Hz, NCHN), 6.15 (2H, s, N(CH)$_2$N of C-boryl ligand), 6.03 (1H, d, $^4J_{HH}$ = 0.8 Hz, NCHC[B]N of imidazole), 5.90 (2H, s, N(CH)$_2$N of N-boryl ligand), 3.25 (4H, sept, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of C-boryl ligand), 2.97 (4H, sept, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of N-boryl ligand), 1.24 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of C-boryl ligand), 1.10 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of N-boryl ligand), 1.06 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of C-boryl ligand), 0.82 (12H, d, $^3J_{HH}$ = 6.9 Hz, CHMe$_2$ of N-boryl ligand). ^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 298 K): δ_C 145.8 (o-C of C-boryl ligand), 145.4 (o-C of N-boryl ligand), 140.5 (i-C of C-boryl ligand), 140.1 (NCHN), 137.6 (i-C of N-boryl ligand), 128.5 (p-C of N-boryl ligand), 127.4 (p-C of C-boryl ligand), 124.8 (NCHC[B]N of imidazole), 124.5 (m-C of N-boryl ligand), 123.6 (m-C of C-boryl ligand), 119.8 (N(CH)$_2$N of C-boryl ligand), 118.9 (N(CH)$_2$N of N-boryl ligand), 28.8 (CHMe$_2$ of C-boryl ligand), 28.7 (CHMe$_2$ of N-boryl ligand), 24.6 (CHMe$_2$ of C-boryl ligand), 24.5 (CHMe$_2$ of N-boryl ligand), 24.1 (CHMe$_2$ of C-boryl ligand), 23.4 (CHMe$_2$ of N-boryl ligand). Boron-bound quaternary carbons were not observed. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 21-24 (overlapping br s, C- and N-boryl ligands). MS (CI): m/z (assignment, %) 841.6 ([M]H$^+$, 2%). Acc. Mass EI: calc. for $C_{55}H_{76}{}^{10}B^{11}BN_4$: 840.6261; found: 840.6276. Elemental microanalysis: found (calc. for $C_{55}H_{75}B_2N_6$): C 76.55 (78.47)%, H 8.64 (8.98)%, N 9.97 (9.98)%.

[(6^{B2})H][BPh$_4$]: A mixture of {(HCDippN)$_2$}BBr (0.15 g, 0.32 mmol), potassium bis(trimethylsilyl)amide (0.06 g, 0.32 mmol) and 4,5-dimethylimidazole (0.03 g, 0.32 mmol) in benzene (10 mL) was stirred for 1 h. Volatiles were removed in vacuo and a further portion of {(HCDippN)$_2$}BBr added (15 mg, 0.32 mmol). After redissolving in

acetonitrile (10 mL), the resulting mixture was stirred for 15 min, whereupon Na[BPh_4] (0.11 g, 0.32 mmol) was added and the solution stirred for a further 15 min. Volatiles were removed in vacuo, and the residue extracted into dichloromethane and filtered. Volatiles were again removed in vacuo and the resulting residue washed with hot hexane (3 x 3 mL) to yield the product as a light brown powder. Yield: 0.12 g, 31%. Single crystals suitable for X-ray crystallography were obtained from a concentrated C_6D_6 solution at room temperature. ^{1}H NMR (MeCN-d_3, 400 MHz, 298 K): δ_H 7.37-7.38 (4H, m, p-H of Dipp), 7.27-7.30 (m, 8H, o-H of [BPh_4]$^-$), 7.16-7.18 (8H, m, m-H of Dipp), 6.98-7.01 (8H, m, m-H of [BPh_4]$^-$), 6.83-6.86 (4H, m, p-H of [BPh_4]$^-$), 6.49 (4H, s, N(CH)$_2$N of boryl ligand), 2.73 (8H, sept, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.85 (6H, s, N(CMe)$_2$N), 1.11 (24H, d, $^3J_{HH}$ = 6.7 Hz, CH<u>Me$_2$</u>), 0.74 (24H, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u>). ^{13}C{^{1}H} NMR (MeCN-d_3, 101 MHz, 298 K): δ_C 164.8 (q, $^1J_{CB}$ = 49.3 Hz, i-C of [BPh_4]$^-$), 145.7 (o-C of boryl ligand), 136.7 (br m, o-C of [BPh_4]$^-$), 135.3 (i-C of Dipp), 132.5 (N(<u>C</u>Me)$_2$N), 130.0 (p-C of Dipp), 129.3 (NCHN), 126.5 (br q, $^3J_{CB}$ = 2.7 Hz, m-C of [BPh_4]$^-$), 125.5 (m-C of Dipp), 122.7 (p-C of [BPh_4]$^-$), 122.2 (N(CH)$_2$N of boryl ligand), 29.4 (<u>C</u>HMe$_2$), 25.7 (CH<u>Me$_2$</u>), 23.3 (CH<u>Me$_2$</u>), 10.4 (N(C<u>Me</u>)$_2$N). ^{11}B NMR (MeCN-d_3, 160 MHz, 298 K): δ_B 20 (br s, boryl ligand), -7 (s, [BPh_4]$^-$). MS (ESI): m/z (assignment, %) 869.7 ([M]$^+$, 97%). Acc. Mass ESI: calc. for $C_{57}H_{79}B_2N_6$: 869.6636; found: 869.6564.

Reaction of [(6^{B2})H][BPh_4] with K[N(SiMe$_3$)$_2$] – generation of 7: [(**6**^{B2})H][BPh_4] (0.03 g, 0.02 mmol) and potassium bis(trimethylsilyl)amide (ca. 0.005 g, 0.02 mmol) were dissolved in benzene (1 mL) and the reaction mixture stirred for 2 h. Volatiles were removed in vacuo and the residue washed with a minimal amount of acetonitrile and dried in vacuo to yield the product as a light brown solid. Yield: ca. 0.006 g, 30%. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ_H 7.17-7.20 (35H, overlapping m, p-H of Dipp of C- or N-boryl ligand and C_6D_5H), 7.08-7.13 (6H, overlapping m, m-H of Dipp of N-boryl ligand and p-H of Dipp of C- and N-boryl ligand), 7.08 (1H, s, NCHN), 7.00-7.01 (4H, m, m-H of Dipp of C-boryl ligand), 6.25 (2H, s, N(CH)$_2$N of N-boryl ligand), 6.11 (2H, s, N(CH)$_2$N of C-boryl ligand), 3.42 (4H, sept, $^3J_{HH}$ = 6.9 Hz, C<u>H</u>Me$_2$ of C- or N-boryl ligand), 3.07 (4H, sept, $^3J_{HH}$ = 6.9 Hz, C<u>H</u>Me$_2$ of C- or N-boryl ligand), 2.06 (2H, s, NCC<u>H</u>$_2$[B]), 1.40 (3H, s, NCMe), 1.20 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand), 1.11 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand), 1.05 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand), 0.94 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K): δ_C 146.9 (o-C of Dipp of C- or N-boryl ligand), 145.7 (o-C of Dipp of C- or N-boryl ligand), 139.5 (i-C of Dipp of N-boryl ligand), 137.5 (overlapping s, NCMe or NCCH$_2$[B] and i-C of Dipp of C-boryl ligand), 137.1 (N<u>C</u>Me or N<u>C</u>CH$_2$[B]), 127.4-128.6 (overlapping signals, p-C of Dipp of C- and N-boryl ligands and C_6D_6), 124.2 (m-C of Dipp of C-boryl ligand), 123.5 (m-C of N-boryl ligand), 122.9 (NCHN), 119.5 (overlapping s, N(CH)$_2$N of C- and N-boryl ligand), 28.8 (<u>C</u>HMe$_2$ of C- or N-boryl ligand), 28.3 (<u>C</u>HMe$_2$ of C- or N-boryl ligand), 25.9 (CH<u>Me$_2$</u> of C- or N-boryl ligand), 25.7 (CH<u>Me$_2$</u> of C- or N-boryl ligand), 23.8 (CH<u>Me$_2$</u> of C- or N-boryl ligand), 23.1 (CH<u>Me$_2$</u> of C- or N-boryl ligand), 10.0 (NC<u>Me</u>). Boron bound quaternary carbon not observed. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 22-29 (br s, boryl ligands). MS (ESI): m/z (assignment, %) 825.6 ([M]$^+$, 8%). Acc. Mass ESI: calc. for $C_{57}H_{78}{}^{10}B_2N_6$: 866.6541; found: 866.6526.

[(8^{BMe})H][OTf]: Method (a): To a solution of **5** (0.50 g, 0.59 mmol) in benzene (20 mL) was added methyl trifluoromethanesulfonate (67 µL, 0.59 mmol) and the resulting mixture stirred for 3 h. The ^{1}H NMR spectrum of an aliquot taken from the reaction mixture at this point indicates full conversion to a new product. Volatiles were removed in vacuo and the residue washed with pentane to yield the crude product as an off-white solid. Yield: 480 mg, 76%. Colourless single crystals suitable for X-ray crystallography could be obtained by layering a benzene solution with pentane. Method (b): A mixture of {(HCDippN)$_2$}BBr (5.00 g, 10.70 mmol), imidazole (0.36 g, 5.30 mmol) and potassium bis(trimethylsilyl)amide (2.10 g, 10.50 mmol) was dissolved in pentane (100 mL) and the reaction mixture stirred overnight. The ^{1}H NMR spectrum of an aliquot taken from the reaction mixture at this point indicates full conversion to **5**. Methyl trifluoromethanesulfonate (0.67 mL, 5.9 mmol) was then added, which resulted in the immediate formation of a white precipitate. The reaction mixture was stirred overnight and filtered. The white solid was washed with pentane (5 x 20 mL) and dried in vacuo yielding the product as a white solid. Yield: 4.80 g, 84%. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ_H 8.57 (1H, br s, NCHN), 7.24-7.28 (2H, m, p-H of N-boryl ligand), 7.07-7.12 (6H, overlapping m, m-H of C-boryl ligand and p-H of N-boryl ligand), 6.91-6.93 (4H, m, m-H of C-boryl ligand), 6.27 (1H, d, $^4J_{HH}$ = 1.4 Hz, NCHC[B]N of imidazole), 6.12 (2H, s, N(CH)$_2$N of C-boryl ligand), 5.90 (2H, s, N(CH)$_2$N of N-boryl ligand), 3.70 (3H, s, NMe), 2.77-2.90 (8H, overlapping m, C<u>H</u>Me$_2$ of C- and N-boryl ligand), 1.10 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u> of N-boryl ligand), 1.00 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u> of C-boryl ligand), 0.96 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of N-boryl ligand), 0.78 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of C-boryl ligand. ^{1}H NMR (toluene-d_8, 400 MHz, 298 K): δ_H 8.54 (br s, 1H, NCHN), 7.23-7.27 (2H, m, p-H of Dipp of N-boryl ligand), 7.08-7.12 (2H, m, p-H of Dipp of C-boryl ligand), 7.05-7.07 (4H, m, m-H of Dipp of N-boryl ligand), 6.90-6.92 (4H, m, m-H of Dipp of C-boryl ligand), 6.25 (1H, d, $^4J_{HH}$ = 1.3 Hz, NCHC[B]N of imidazole), 6.12 (2H, s, N(CH)$_2$N of C-boryl ligand), 5.93 (2H, s, N(CH)$_2$N of N-boryl ligand), 3.65 (3H, s, NMe), 2.75-2.85 (8H, overlapping m, C<u>H</u>Me$_2$ of C- and N-boryl ligand), 1.10 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u> of N-boryl ligand), 1.01 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u> of C-boryl ligand), 0.94 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of N-boryl ligand), 0.77 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me$_2$</u> of C-boryl ligand). ^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 298 K): δ_C 145.1 (o-C of Dipp of N-boryl ligand), 144.7 (o-C of Dipp of C-boryl ligand), 141.3 (NCHN), 136.9 (i-C of Dipp of C-boryl ligand), 135.0 (i-C of Dipp of N-boryl ligand), 129.8 (p-C of Dipp of N-boryl ligand), 128.7 (p-C of Dipp of C-boryl ligand), 126.7 (N<u>C</u>HC[B]N of imidazole), 125.3 (m-C of Dipp of N-boryl ligand), 124.6 (m-C of Dipp of C-boryl ligand), 121.5 (N(CH)$_2$N of C-boryl ligand), 120.3 (N(CH)$_2$N of N-boryl ligand), 37.2 (NMe), 28.9 (<u>C</u>HMe$_2$ of N-boryl ligand), 28.7 (<u>C</u>HMe$_2$ of C-boryl ligand), 25.5 (CH<u>Me$_2$</u> of C-boryl ligand), 24.8 (CH<u>Me$_2$</u> of N-boryl ligand), 23.8 (CH<u>Me$_2$</u> of N-boryl ligand), 23.2 (CH<u>Me$_2$</u> of C-boryl ligand). Boron-bound quaternary carbons not observed. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 19 (br s, C- and N-boryl ligands). ^{19}F NMR (C_6D_6, 377 MHz, 298 K): δ_F -77.63. MS (ESI): m/z (assignment, %) 841 ([M]$^+$, 96%). Acc. Mass ESI: calc. for $C_{56}H_{77}B_2N_6$: 855.6408; found: 855.6525. Elemental microanalysis: found (calc. for $C_{57}H_{77}B_2F_3N_6O_3S$): C 67.79 (68.13)%, H 7.86 (7.72)%, N 8.23 (8.36)%.

In situ generation of 8^{BMe}: A mixture of [(**8**^{BMe})H][OTf] (0.04 g, 0.04 mmol) and potassium bis(trimethylsilyl)amide (0.01 g, 0.05 mmol) in a J. Young's NMR tube was dissolved in toluene-d_8 (0.5 mL) at -78 °C and the tube shaken intermittently at -78 °C. The resulting precipitate was collected at the top of the tube using a centrifuge. The in situ ^{1}H and ^{13}C NMR spectra measured immediately show clean conversion to the free carbene, which is stable in solution at -80 °C but rearranges with a half-life of ca. 4 h at room temperature. ^{1}H NMR (toluene-d_8, 400 MHz, 283 K): δ_H 7.07-7.16 (5H, overlapping m, p-H of Dipp of C- and N-boryl ligand and $C_6D_4HCD_3$), 6.94-7.02 (9H, overlapping m, m-H of Dipp of C- and N-boryl ligand and $C_6D_4HCD_3$), 6.23 (1H, s, NCHC[B]N of imidazole), 6.17 (2H, s, N(CH)$_2$N of C- or N-boryl ligand), 5.97 (2H, s, N(CH)$_2$N of C- or N-boryl ligand), 3.15-3.21 (7H, overlapping m, C<u>H</u>Me$_2$ of C- or N-boryl ligand and NMe), 3.02 (4H, br m, C<u>H</u>Me$_2$ of C- or N-boryl ligand), 1.19 (12H, d, $^3J_{HH}$ = 6.4 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand, 1.08 (12H, d, $^3J_{HH}$ = 6.4 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand), 0.99 (12H, d, $^3J_{HH}$ = 6.4 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand), 0.80 (12H, d, $^3J_{HH}$ = 6.4 Hz, CH<u>Me$_2$</u> of C- or N-boryl ligand). ^{13}C{^{1}H} NMR (toluene-d_8, 126 MHz, 298 K): δ_C 225.8 (br s, NCN), 146.2 (o-C of Dipp of C- or N-boryl ligand), 145.4 (o-C of Dipp of C- or N-boryl ligand), 140.0 (i-C of Dipp of C- or N-boryl ligand),

139.3 (i-C of Dipp of C- or N-boryl ligand), 128.5-127.9 (overlapping signals, p-C of C- or N-boryl ligand and toluene-d_8), 127.9 (p-C of C- or N-boryl ligand), 127.6 (NCHC[B]N of imidazole), 124.5 (m-C of C- or N-boryl ligand), 124.1 (m-C of C- or N-boryl ligand), 120.8 ($N(CH)_2N$ of C- or N-boryl ligand), 119.4 ($N(CH)_2N$ of C- or N-boryl ligand), 38.5 (NMe), 29.3 ($CHMe_2$ of C- or N-boryl ligand), 29.0 ($CHMe_2$ of C- or N-boryl ligand), 25.8 ($CHMe_2$ of C- or N-boryl ligand), 25.1 ($CHMe_2$ of C- or N-boryl ligand), 24.2 ($CHMe_2$ of C- or N-boryl ligand), 23.7 ($CHMe_2$ of C- or N-boryl ligand). Boron-bound quaternary carbon not observed. ^{11}B NMR (toluene-d_8, 128 MHz, 253 K): δ_B 22 (br, C- and N-bound boryl ligands).

9: A mixture of [(**8**^{BMe})H][OTf] (0.30 g, 0.03 mmol) and potassium bis(trimethylsilyl)amide (0.06 g, 0.03 mmol) was dissolved in benzene (10 mL) and the resulting solution stirred at 80 °C for 20 min. After filtration, volatiles were removed in vacuo and the residue dissolved in a minimal amount of acetonitrile at 80 °C. The solution was allowed to cool slowly in the oil bath, producing colourless needle-like crystals. After filtration, the crystals were washed with acetonitrile (4 x 5 mL) to yield the product as a white crystalline solid. Yield: 0.12 g, 45%. Colourless single crystals suitable for X-ray crystallography were grown from diethyl ether at -20 °C. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ_H 7.09-7.16 (4H, overlapping m, p-H of Dipp of C2- and C4-boryl ligand), 7.03-7.05 (4H, m, m-H of Dipp of C2-boryl ligand), 6.98-7.00 (4H, m, m-H of Dipp of C4-boryl ligand), 6.72 (1H, s, NCHC[B]N of imidazole), 6.27 (2H, s, $N(CH)_2N$ of C2-boryl ligand), 6.20 (2H, s, $N(CH)_2N$ of C4-boryl ligand), 3.31 (4H, sept, $^3J_{HH}$ = 6.8 Hz , $CHMe_2$ of C2-boryl ligand), 3.10 (4H, sept, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C4-boryl ligand), 2.94 (3H, s, NMe), 1.20 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C4-boryl ligand), 1.16 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C2-boryl ligand), 1.07 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C2-boryl ligand), 0.82 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C4-boryl ligand). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): δ_C 145.9 (o-C of Dipp of C2-boryl ligand), 145.7 (o-C of Dipp of C4-boryl ligand), 140.6 (NCHC[B]N of imidazole), 139.4 (i-C of Dipp of C4-boryl ligand), 138.8 (i-C of Dipp of C2-boryl ligand), 128.4 (NC[B]N), 127.6 and 127.8 (p-C of Dipp of C2- and C4-boryl ligand), 124.0 (m-C of Dipp of C4-boryl ligand), 123.6 (m-C of Dipp of C2-boryl ligand), 120.3 (overlapping s, $N(CH)_2N$ of C2- and C4-boryl ligand), 34.4 (NMe), 28.7 ($CHMe_2$ of C2-boryl ligand), 28.6 ($CHMe_2$ of C4-boryl ligand), 25.8 ($CHMe_2$ of C2-boryl ligand), 25.6 ($CHMe_2$ of C4-boryl ligand), 23.5 ($CHMe_2$ of C2-boryl ligand), 23.2 ($CHMe_2$ of C4-boryl ligand). Boron-bound quaternary carbons not observed. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 23 (br s, C- and N-boryl ligands). MS (EI): m/z (assignment, %) 854.6 ($[M]^+$, 9%). Acc. Mass EI: calc. for $C_{56}H_{76}{}^{10}B_2N_6$: 852.6385; found: 852.6364. Elemental microanalysis: found (calc. for $C_{56}H_{76}B_2N_6$): C 78.83 (78.68)%, H 8.61 (8.96)%, N 9.74 (9.83)%.

In situ generation of 3^{BMe}: A mixture of [(**3**^{BMe})H][OTf] (0.03 g, 0.06 mmol) and potassium bis(trimethylsilyl)amide (0.01 g, 0.07 mmol) in a J. Young's NMR tube was dissolved in C_6D_6 (0.5 mL) and the tube shaken. The resulting precipitate was collected at the top of the tube using a centrifuge. The in situ ^1H and ^{13}C NMR spectra measured immediately show clean conversion to the free carbene, which is stable in solution at -80 °C but rearranges with a half-life of ca. 49 h at room temperature. ^1H NMR (C_6D_6, 500 MHz, 298 K): δ_H 7.19-7.22 (2H, m, p-H of Dipp), 7.13-7.16 (4H, m, m-H of Dipp), 6.43 (1H, s, NCHCHN of imidazole), 6.09 (2H, s, $N(CH)_2N$ of boryl ligand), 5.94 (1H, s, NCHCHN of imidazole), 3.34 (4H, sept, $^3J_{HH}$ = 7.0 Hz, $CHMe_2$), 3.09 (3H, s, NMe), 1.23 (12H, d, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$), 1.19 (12H, d, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 298 K): δ_C 223.6 (NCN), 146.4 (o-C of Dipp), 139.4 (i-C of Dipp), 127.9-128.3 (overlapping signals, p-C of Dipp and C_6D_6) 123.9 (m-C of Dipp), 120.9 and 119.7 (NCHCHN), 119.0 ($N(CH)_2N$ of boryl ligand), 37.4 (NMe), 28.9 ($CHMe_2$), 24.7 ($CHMe_2$), 23.6 ($CHMe_2$). ^{11}B NMR (C_6D_6, 160 MHz, 298 K): δ_B 23 (b s, boryl ligand).

10: To a mixture of [(**8**^{BMe})H][OTf] (0.50 g, 0.47 mmol), sodium bis(trimethylsilyl)amide (0.09 g, 0.51 mmol) and selenium powder (0.15 g, 1.9 mmol) was added benzene (7 mL), and the resulting mixture stirred at room temperature for 1 h. After filtration, the volume of the filtrate was reduced until the onset of precipitation. The solution was then warmed until all the precipitate dissolved, and the solution then allowed to cool slowly to room temperature in the oil bath, producing colourless single crystals suitable for X-ray crystallography. After filtration, the remaining crystals were dried in vacuo to yield the product as a white solid. Yield: 0.29 g, 66 %. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ_H 7.17-7.21 (12H, overlapping m, p-H of Dipp of C-boryl ligand and C_6D_5H), 7.08 (6H, overlapping m, p-H and m-H of Dipp N-boryl ligand), 6.93 (4H, m, m-H of Dipp of C-boryl ligand), 6.32 (1H, s, NCHC[B]N of imidazole), 6.21 (2H, s, $N(CH)_2N$ of N-boryl ligand), 6.16 (2H, s, $N(CH)_2N$ of C-boryl ligand), 3.64 (4H, br m, $CHMe_2$ of N-boryl ligand), 3.20 (3H, s, NMe), 2.99 (4H, sept, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C-boryl ligand), 1.17 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C-boryl ligand), 1.12 (12H, br m, $CHMe_2$ of C-boryl ligand), 1.05 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of N-boryl ligand), 0.69 (12H, d, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$ of N-boryl ligand). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 298K): δ_C 163.7 (CSe), 146.6 (o-C of Dipp of C-boryl ligand), 144.7 (o-C of Dipp of N-boryl ligand), 138.0 (i-C of Dipp of C-boryl ligand), 137.3 (i-C of Dipp of N-boryl ligand), 128.4-127.9 (overlapping signals, C_6D_6, p-C of Dipp of C-boryl ligand and p-C or m-C of Dipp of N-boryl ligand), 125.0 (NCHC[B]N of imidazole), 124.4 (m-C of Dipp of C-boryl ligand), 124.0 (p-C or m-C of Dipp N-boryl ligand), 120.8 ($N(CH)_2N$ of C-boryl ligand), 119.9 ($N(CH)_2N$ of N-boryl ligand), 36.8 (NMe), 28.7 ($CHMe_2$ of boryl ligand), 28.5 ($CHMe_2$ of boryl ligand), 26.6 ($CHMe_2$ of C-boryl ligand), 25.4 ($CHMe_2$ of N-boryl ligand), 24.0 ($CHMe_2$ of C-boryl ligand), 23.1 ($CHMe_2$ of N-boryl ligand). Boron bound quaternary carbon not observed. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ_B 22 (br s, C- and N-boryl ligands). ^{77}Se NMR (Acetone-d_6, 95 MHz, 298 K): δ_{Se} 67. MS (EI): m/z (assignment, %) 934.6 ($[M]^+$, 3%). Acc. Mass EI: calc. for $C_{56}H_{76}{}^{10}B^{11}BN_6Se$: 954.5519; found: 954.5595. Elemental microanalysis: found (calc. for $C_{56}H_{76}B_2N_6Se$): C 71.72 (72.03)%, H 8.32 (8.20)%, N 9.20 (9.00)%.

(8^{BMe})AuCl: A mixture of [(**8**^{BMe})H][OTf] (0.31 g, 0.29 mmol) and potassium bis(trimethylsilyl)amide (0.06 g, 0.29 mmol) was dissolved in toluene at -40 °C and the resulting solution stirred for 20 min. The cloudy solution was then filtered onto (THT)AuCl (0.09 g, 0.29 mmol), and the resulting mixture stirred at -40 °C for 30 min before being allowed to slowly warm to room temperature. Volatiles were removed in vacuo and the residue dissolved in a minimal amount of acetonitrile at 80 °C. The solution was allowed to cool slowly to room temperature producing colourless crystals. After filtration, the crystals were washed three times with a minimal amount of acetonitrile, and then dried in vacuo to yield the product as a white solid. Further crops of the product could be obtained by recrystallization from a concentrated solution of the filtrate stored at -20 °C. Yield: 0.11 g, 34%. Colourless single crystals suitable for X-ray crystallography were grown from a concentrated solution in hexane. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ_H 7.12-7.16 (5H, overlapping m, p-H of Dipp of N-boryl ligand and C_6D_5H), 7.05-7.09 (2H, m, p-H of Dipp of C-boryl ligand), 6.98-7.00 (4H, m, m-H of Dipp of N-boryl ligand), 6.88-6.90 (4H, m, m-H of Dipp of C-boryl ligand), 6.37 (1H, s, NCHC[B]N of imidazole), 6.14 (2H, s, $N(CH)_2N$ of N-boryl ligand), 6.08 (2H, s, $N(CH)_2N$ of C-boryl ligand), 3.61 (4H, br m, $CHMe_2$ of N-boryl ligand), 2.94 (3H, s, NMe), 2.85 (4H, sept, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C-boryl ligand), 1.30-1.21 (24H, overlapping m, $CHMe_2$ of N-boryl ligand), 1.01 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$ of C-boryl ligand), 0.46 (12H, d, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$ of C-boryl ligand). ^1H NMR (C_6D_6, 400 MHz, 333 K): δ_H 7.12-7.16 (5H, overlapping m, p-H of Dipp of N-boryl ligand and C_6D_5H), 7.06-7.10 (2H, m, p-H of Dipp of C-boryl ligand), 7.00-7.02 (4H, m, m-H of Dipp of N-boryl ligand), 6.90-6.91 (4H, m, m-H of Dipp of C-boryl ligand), 6.37 (1H, s, NCHC[B]N of imidazole), 6.15 (2H, s, $N(CH)_2N$ of N-boryl ligand), 6.10

(2H, s, $N(CH)_2N$ of C-boryl ligand), 3.60 (4H, sept, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me_2 of N-boryl ligand), 3.00 (3H, s, NMe), 2.86 (4H, sept, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me_2 of C-boryl ligand), 1.18-1.21 (24H, overlapping d, CH<u>Me</u>$_2$ of N-boryl ligand), 1.01 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH<u>Me</u>$_2$ of C-boryl ligand), 0.50 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH<u>Me</u>$_2$ of C-boryl ligand). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 333 K): δ_C 177.0 (NCN), 146.8 (o-C of Dipp of N-boryl ligand), 144.6 (o-C of Dipp of C-boryl ligand), 137.7 (i-C of Dipp of C-boryl ligand), 136.5 (i-C of Dipp of N-boryl ligand), 127.8-128.3 (overlapping s, p-C of Dipp of C-boryl and N-boryl ligands), 127.6 (N<u>C</u>HC[B]N of imidazole), 124.6 (m-C of Dipp of C-boryl ligand), 124.0 (m-C of Dipp of N-boryl ligand), 120.9 $(N(CH)_2N$ of N-boryl ligand), 120.3 $(N(CH)_2N$ of C-boryl ligand), 37.8 (NMe), 29.2 (<u>C</u>HMe_2 of N-boryl ligand), 28.5 (<u>C</u>HMe_2 of C-boryl ligand), 26.3 (CH<u>Me</u>$_2$ of N-boryl ligand), 25.2 (CH<u>Me</u>$_2$ of C-boryl ligand), 24.5 (CH<u>Me</u>$_2$ of N-boryl ligand), 23.0 (CH<u>Me</u>$_2$ of C-boryl ligand). Boron bound quaternary carbons not observed. ^{11}B NMR (C_6D_6, 128 MHz, 333 K): δ_B 22 (br s, C- and N-boryl ligands). MS (EI): m/z (assignment, %) 1086.6 ($[M]^+$, 3%). Acc. Mass EI: calc. for $C_{56}H_{76}{}^{10}B_2N_6AuCl$: 1084.5739; found: 1084.5776. Elemental microanalysis: found (calc. for $C_{56}H_{76}B_2N_6AuCl$): C 61.66 (61.86)%, H 7.23 (7.05)%, N 7.84 (7.73)%.

***Cis*-(8^{BMe})Rh(CO)$_2$Cl:** Method (a) (in situ): (**8**^{BMe})Rh(cod)Cl (0.03 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL) in a J. Young's NMR tube and the solution degassed via three freeze-pump-thaw cycles prior to backfilling the tube with CO. The ^1H NMR spectrum measured at this point indicated complete conversion to cis-(**10**^{BMe})Rh(CO)$_2$Cl. Method (b) (preparative scale): A mixture of [(**8**^{BMe})H][OTf] (0.40 g, 0.37 mmol) and potassium bis(trimethylsilyl)amide (0.08 g, 0.37 mmol) was dissolved in benzene (10 mL) and the resulting mixture stirred for 5 min at room temperature. The cloudy solution was then filtered onto solid $[Rh(CO)_2Cl]_2$ (66 mg, 0.17 mmol) and the resulting mixture stirred for 10 min. The ^1H NMR spectrum of an aliquot taken from the solution at this point indicated complete conversion to the desired product (with < 5% impurities). Volatiles were removed in vacuo and the residue dissolved in hot hexane. The resulting solution was allowed to cool slowly to room temperature in the oil bath and then further cooled to -20 °C to yield a crystalline product. Isolated yields of the product were very low due to the high solubility of the product in compatible media. Single crystals suitable for X-ray crystallography were obtained by recrystallization from hexane at -20 °C. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ_H 6.98-7.16 (21H, overlapping m, p-H and m-H of Dipp and C_6D_5H), 6.59 (1H, s, NCHC[B]N of imidazole), 6.21 (2H, s, $N(CH)_2N$ of C-boryl ligand), 6.18 (2H, br s, $N(CH)_2N$ of N-boryl ligand), 4.02 (3H, s, NMe), 3.26 (4H, br m, C<u>H</u>Me_2 of N-boryl ligand), 2.98 (4H, br m, C<u>H</u>Me_2 of C-boryl ligand), 0.72-1.36 (62H, overlapping m, CH<u>Me</u>$_2$ and n-hexane solvate). ^1H NMR (C_6D_6, 400 MHz, 343 K): δ_H 7.12-7.18 (20H, overlapping m, p-H of Dipp and C_6D_5H), 7.06-7.08 (4H, m, m-H of Dipp of N-boryl ligand), 7.00-7.02 (4H, m, m-H of Dipp of C-boryl ligand), 6.59 (1H, s, NCHC[B]N of imidazole), 6.20 (2H, s, $N(CH)_2N$ of C-boryl ligand), 6.17 (2H, br s, $N(CH)_2N$ of N-boryl ligand), 3.98 (3H, s, NMe), 3.22 (4H, br m, C<u>H</u>Me_2 of N-boryl ligand), 2.99 (4H, sept, $^3J_{HH}$ = 6.9 Hz, C<u>H</u>Me_2 of C-boryl ligand), 1.23-1.29 (8H, overlapping m, CH_2 of n-hexane solvate), 1.03-1.13 (42H, overlapping d, CH<u>Me</u>$_2$), 0.88 (6H, t, $^3J_{HH}$ = 6.8 Hz, CH_3 of n-hexane solvate). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 343 K): δ_C 187.5 (d, $^2J_{RhC}$ = 55.0 Hz, RhCO), 182.5-183.5 (overlapping d, RhCO and NCN), 145.5 (o-C of Dipp of N-boryl ligand), 145.4 (o-C of Dipp of C-boryl ligand), 138.4 (i-C of Dipp of N-boryl ligand), 137.8 (i-C of Dipp of C-boryl ligand), 129.4 (N<u>C</u>HC[B]N of imidazole), 127.8-128.3 (overlapping signals, p-C of Dipp and C_6D_6), 125.0 (m-C of Dipp of N-boryl ligand), 124.2 (m-C of Dipp of C-boryl ligand), 121.3 $(N(CH)_2N$ of C-boryl ligand), 120.3 $(N(CH)_2N$ of N-boryl ligand), 39.9 (NMe), 31.9 (CH_2 of n-hexane solvate), 28.8 (<u>C</u>HMe_2 of C-boryl ligand), 28.7 (<u>C</u>HMe_2 of N-boryl ligand), 26.0 (CH<u>Me</u>$_2$ of C-boryl ligand), 25.8 (br s, CH<u>Me</u>$_2$ of N-boryl ligand), 23.7 (CH<u>Me</u>$_2$ of C-boryl ligand), 23.5 (br s, CH<u>Me</u>$_2$ of N-boryl ligand), 23.0 (CH_2 of n-hexane solvate), 14.2 (CH_3 of n-hexane solvate). Boron bound quaternary carbons not observed. ^{11}B NMR (C_6D_6, 128 MHz, 343 K): δ_B 21-23 (br s, C- and N-boryl ligands). IR (CH_2Cl_2): 1990 (s, C–O stretch) and 2069 (s, C–O stretch) cm^{-1}. Elemental microanalysis: found (calc. for $C_{58}H_{76}RhB_2ClN_6O_2$): C 66.38 (66.39)%, H 7.61 (7.30)%, N 8.33 (8.01)%.

Crystallography

Single-crystal X-ray diffraction data for all compounds (except *cis*-(**10**^{BMe})Rh(CO)$_2$Cl) were collected on a Nonius KappaCCD diffractometer using Mo K_α radiation (λ = 0.71073 Å) or on an Oxford Diffraction Supernova diffractometer using mirror monochromated Cu K_α radiation (λ = 1.5418 Å) at 150 K. Crystals were selected under Paratone-N or perfluoropolyether oil, mounted on MiTeGen loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[32] Data collection and reduction were carried out using Collect and Denzo/Scalepack (Nonius KappaCCD)[33] or the CrysAlisPro package (Oxford Diffraction Supernova).[34] Structures were subsequently solved using SHELXT[35] and refined on F^2 using the SHELXL 2018 package and the graphical interface Olex2 or X-Seed.[36-38] X-ray diffraction data for *cis*-(**10**^{BMe})Rh(CO)$_2$Cl were collected using beamline I19-1 at Diamond Light Source at 100 K using a Dectris Pilatus 2M pixel-array photon-counting detector,[39] and data were reduced using XIA2.[40] The structure of *cis*-(**10**^{BMe})Rh(CO)$_2$Cl was solved *ab initio* from the integrated intensities using SHELXT,[35] and refined using full-matrix least-squares refinement with CRYSTALS.[41-43] PLATON/SQUEEZE[44,45] was used to model diffuse scattering in the void space. CCDC numbers: 1867712-1867724 and 1868625.

DFT calculations

All computational work reported here utilized density functional theory (DFT). Calculations of ground state structure/energetics on the isomers of compound **5** and on compound **8**^{BMe} were performed using the Amsterdam Density Functional (ADF) 2014 software package. Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke,[46] and correlation correction from Perdew.[47] Slater-type orbitals (STOs) were used for the triple zeta basis set with an additional set of polarization functions (TZP).[48] The full-electron basis set approximation was applied with no molecular symmetry. General numerical quality was good. Geometric details and molecular orbital energies were obtained after unrestricted geometry optimization. Mechanistic calculations on the rearrangement of **8**^{BMe} to **10** were performed with Gaussian09 (Revision D.01) program package[49] using the PBE1PBE hybrid exchange-correlation functional[50] in combination with def-TZVP basis set[51] and the polarizable continuum solvent model (pcm, toluene).[52] In addition, Grimme's empirical dispersion correction scheme was employed to treat dispersion effects.[48] The nature of all stationary points (minimum or saddle point) was confirmed by full frequency calculations.

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Keywords: N-heterocyclic carbene • boryl group • boron • rearrangement • metal complex

[1] (a) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463–6466; (b) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363

[2] See, for example: (a) A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913-921; (b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39-92; (c) F. E. Hahn, M.C. Jahnke, *Angew. Chem., Int. Ed.* **2008**, *47*, 3122-3172; (d) T. Dröge, F. Glorius, *Angew. Chem., Int. Ed.* **2010**, *49*, 6940-6952; (e) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304-5313; (f) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.

[3] See, for example: (a) W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1290-1309; (b) S. Würtz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523-1533; (c) R. Corberán, E. Mas-Márza, E. Peris, *Eur. J. Inorg. Chem.* **2009**, 1700-1716; (d) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561-3598; (e) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676.

[4] For a very recent review of electronic structure in carbene complexes, see: D. Munz, *Organometallics* **2018**, *37*, 275-289.

[5] (a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113-115; (b) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069-16079; (c) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *Chem. Lett.* **2008**, *37*, 802-803.

[6] For reviews of metal boryl chemistry see, for example: (a) G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, *Chem. Rev.* **1998**, *98*, 2685-2722; (b) D.L. Kays, S. Aldridge, *Struct. Bonding (Berlin)* **2008**, *130*, 29-122; (d) L. Dang, Z. Lin, T.B. Marder, *Chem. Commun.* **2009**, 3987-3995; (e) H. Braunschweig, R.D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924-3957: (d) L. Weber, *Eur. J. Inorg. Chem.* **2017**, 3461-3488.

[7] (a) L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.* **2011**, *133*, 3836-3839; (b) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500-6503; (c) A. V. Protchenko, D. Dange, A. D. Schwarz, C. Y. Tang, N. Phillips, P. Mountford, C. Jones, S. Aldridge, *Chem. Commun.* **2014**, *50*, 3841-3844; (d) A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Nature Chem.* **2014**, *6*, 315-319; (e) A. V. Protchenko, D. Dange, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2014**, *136*, 10902-10905; (f) R. Frank, J. Howell, R. Tirfoin, D. Dange, C. Jones, D.M.P. Mingos, S. Aldridge, *J. Am. Chem. Soc.* **2014**, *136*, 15730-15741; (g) A. V. Protchenko, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford, S. Aldridge, *Organometallics* **2015**, *34*, 2126-2129; (h) R. Frank, J. Howell, J. Campos, R. Tirfoin, N. Phillips, S. Zahn, D.M.P. Mingos, S. Aldridge, *Angew. Chem., Int. Ed.* **2015**, *54*, 9586-9590; (i) A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 4555-4559; (j) A. Rit, J. Campos, H. Niu, S. Aldridge, *Nature Chem.* **2016**, *8*, 1022-1026; (k) A. V. Protchenko, J. Urbano, J. A. B. Abdalla, J. Campos, D. Vidovic, A. D. Schwarz, M. P. Blake, P. Mountford, C. Jones, S. Aldridge, *Angew. Chem., Int. Ed.* **2017**, *56*, 15098-15102.

[8] (a) T.J. Hadlington, J.A.B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.* **2016**, *52*, 1717-1720. See also: (b) B. A. Clough, S. Mellino, E. Clot, P. Mountford, *J. Am. Chem. Soc.* **2017**, *139*, 11165-11183; (c) B. A. Clough, S. Mellino, A. V. Protchenko, M. Slusarczyk, L. C. Stevenson, M. P. Blake, B. Xie, E. Clot, P. Mintford, *Inorg. Chem.* **2017**, *56*, 10794-10814.

[9] (a) A. Wacker, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 843-849; (b) A. Weiss, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2002**, 1607-1614; (c) K. E. Krahulic, G. D. Enright, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2005**, *127*, 4142–4143; (d) C. Pra, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2005**, *127*, 10182–10183; (e) F. Lavigne, E. Maerten, G. Alcaraz, N. Saffon-Merceron, C. Acosta-Silva, A. Baceiredo, *J. Am. Chem. Soc.* **2010**, *132*, 8864–8865; (f) Y. Ishida, B. Donnadieu, G. Bertrand, *Proc. Natl. Acad. Sci.* USA **2006**, *103*, 13585-13588. See also (g) W. C. Liu, Y. H. Liu, T. S. Lin, S. M. Peng, C. W. Chiu, *Inorg. Chem.* **2017**, *56*, 10543–10548

[10] D. Herrmannsdorfer, M. Kaaz, O. Puntigam, J. Bender, M. Nieger, D. Gudat, *Eur. J. Inorg. Chem.* **2015**, 4819–4828.

[11] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.

[12] J. W. Storer, K. N. Houk, *J. Am. Chem. Soc.***1993**, *115*, 10426–10427.

[13] M. T. H. Liu, *Acc. Chem. Res.* **1994**, *27*, 287–294.

[14] S. Sole, H. Gornitzka, O. Guerret, G. Bertrand, *J. Am. Chem. Soc.* **1998**, *120*, 9100–9101.

[15] C. Heinemann, W. Thiel, *Chem. Phys. Lett.* **1994**, *217*, 11–16.

[16] X. Cattoën, H. Gornitzka, F. S. Tham, K. Miqueu, D. Bourissou, G. Bertrand, *Eur. J. Org. Chem.* **2007**, 912–917.

[17] G. A. McGibbon, C. Heinemann, D. J. Lavorato, H. Schwarz, *Angew. Chem. Int. Ed.* **1997**, *36*, 1478–1481.

[18] G. Maier, J. Endres, H. P. Reisenauer, *Angew. Chem., Int. Ed.* **1997**, *36*, 1709-1712.

[19] $\%V_{bur}$: (a) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322-4326; (b) L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, *J. Organomet. Chem.* **2005**, *690*, 5407-5413; (c) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759-1766; (d) F. Ragone, A. Poater, L. Cavallo, *J. Am. Chem. Soc.* **2010**, *132*, 4249-4258; (e) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841-861; (f) L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286-2293; (g) A. Gómez-Suárez, D. J. Nelson, S. P. Nolan, *Chem. Commun.* **2017**, *53*, 2650–2660.

[20] D. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.* **2009**, *109*, 3385–3407.

[21] J. J. Dunsford, K. J. Cavell, B. M. Kariuki, *Organometallics* **2012**, *31*, 4118–4121.

[22] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348.

[23] A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667.

[24] R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202–210.

[25] M. Iglesias, D. J. Beetstra, B. Kariuki, K. J. Cavell, A. Dervisi, I. A. Fallis, *Eur. J. Inorg. Chem.* **2009**, 1913–1919.

[26] A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272.

[27] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943.

[28] H. Niu, R. Mangan, A. V. Protchenko, N. Phillips, W. Unkrig, C. Friedmann, E. L. Kolychev, R. Tirfoin, J. Hicks, S. Aldridge, *Dalton Trans*, **2018**, *47*, 7445-7455.

[29] R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray, J. P. Fackler, *Inorg. Synth.* **1989**, *26*, 85-91.

[30] G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1990**, *28*, 88-90.

[31] C. S. Berre, M. Etienne, J. Daran, P. Kalck, *Eur. J. Inorg. Chem.* **2001**, 2689–2697

[32] J. Cosier, A. M. Glazer, *J. Appl. Cryst.* **1986**, *19*, 105–107.

[33] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, *Methods Enzymol.* **1997**, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.

[34] CrysAlisPro v.1.171.35.8 (Agilent Technologies, **2011**).

[35] G. M. Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.

[36] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.

[37] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[38] L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189–191.

[39] D. R. Allan, H. Nowell, S. A. Barnett, M. R. Warren, A. Wilcox, J. Christensen, L. K. Saunders, A. Peach, M. T. Hooper, L. Zaja, S. Patel, L. Cahill, R. Marshall, S. Trimnell, A. J. Foster, T. Bates, S. Lay, M. A. Williams, P. V. Hathaway, G. Winter, M. Gerstel, R. W. Wooley, *Crystals* **2017**, *7*, 336.

[40] (a) P. Evans, *Acta Cryst.* **2006**, *D62*, 72-82; (b) G. Winter, *J. Appl. Cryst.* **2010**, *43*, 186-190; (c) M. D. Winn, C. C. Ballard, K. D. Cowtan, E. J. Dodson, P. Emsley, P. R. Evans, R. M. Keegan, E. B. Krissinel, A. G. W. Leslie, A. McCoy, S. J. McNicholas, G. N. Murshudov, N. S. Pannu, E. A. Potterton, H. R. Powell, R. J. Read, A. Vagin and K. S. Wilson, *Acta Cryst.* **2011**, *D67*, 235-242; (d) P. R. Evans, G. N. Murshudov, *Acta Cryst.* **2013**, *D69*, 1204-1214.

[41] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Cryst.* **2003**, *36*, 1487.

[42] P. Parois, R. I. Cooper, A. L. Thompson, *Chem. Cent. J.* **2015**, *9*, 30.

[43] R. I. Cooper, A. L. Thompson, D. J. Watkin, *J. Appl. Cryst.* **2010**, *43*, 1100-1107.

[44] A. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.

[45] P. van der Sluis, A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194-201.

[46] A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.

[47] J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.

[48] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104-154119; (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, **2009**.

[50] (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868; (b) J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982-9985; (c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170; (d) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.

[51] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835.

[52] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3094.

FULL PAPER

Attempts to access NHCs featuring the diazaborolyl group, {(HCNDipp)$_2$B}, as the N-bound substituent(s) are reported. These are characterized by facile N-to-C migration, although in the cases of imidazolium systems bearing one diazaborolyl and one Me substituent, the target carbenes can be characterized *in situ* by NMR measurements, and trapped by reactions with metal fragments and elemental selenium.

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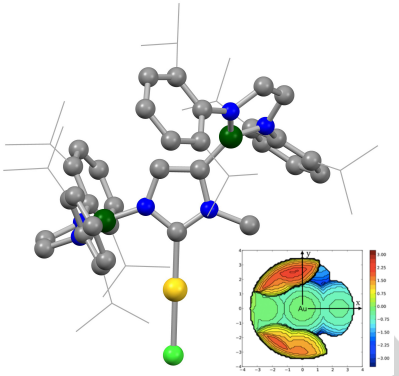

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