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# Metal-free dehydrogenation of amine–boranes by an *N*-heterocyclic carbene†

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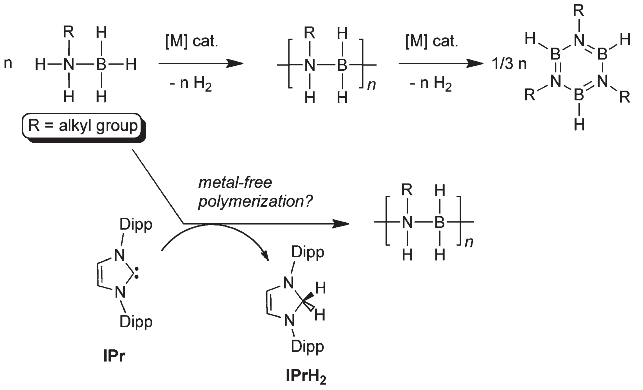
The dehydrogenation of primary and secondary amine–boranes ($RNH_2{\cdot}BH_3$ and $R_2NH{\cdot}BH_3$; R = alkyl groups) was studied using the bulky *N*-heterocyclic carbene IPr (IPr = [(HCNDipp)C:]; Dipp = 2,6-$^iPr_2C_6H_3$) as a stoichiometric dehydrogenation agent. In the case of primary amine–boranes, carbene-bound adducts $IPr{\cdot}BH_2–NH(R)–BH_3$ were obtained in place of the desired polymers $[RNH–BH_2]_n$. The secondary amine–borane $^iPr_2NH{\cdot}BH_3$ participated in dehydrogenation chemistry with IPr to afford the aminoborane $[^iPr_2N{=}BH_2]$ and the dihydroaminal $IPrH_2$ as products. Attempts to induce $H_2$ elimination from the aryl-amine–borane $DippNH_2{\cdot}BH_3$ yielded a reaction mixture containing the known species $IPr{\cdot}BH_2NHDipp$, $IPr{\cdot}BH_2NH(Dipp)–BH_3$, free $DippNH_2$ and $IPrH_2$. The new hindered aryl-amine borane adduct $Ar^*NH_2{\cdot}BH_3$ [$Ar^*$ = 2,6-$(Ph_2CH)_2$-4-$MeC_6H_2$] underwent a reaction with IPr to give $IPr{\cdot}BH_3$ and free $Ar^*NH_2$, consistent with the presence of a weaker N–B dative bond in $Ar^*NH_2{\cdot}BH_3$ relative to its less hindered amine–borane analogues.

## Introduction

Amine–boranes ($R_3N{\cdot}BH_3$; R = alkyl, aryl or H) represent a widely explored chemical class[1] with considerable recent attention devoted to the study of the parent system $H_3N{\cdot}BH_3$ as a chemical source of $H_2$ for fuel cell technologies.[2] In addition, lithium amidoborate salts $Li[NR_2BH_3]$ have been used in organic chemistry as easy-to-handle and selective reducing ($H^-$) agents.[3] Recently, the Manners group reported the synthesis of novel linear B–N polymers $[RNH–BH_2]_n$ *via* the controlled dehydrogenative coupling of primary amine–boranes, such as $MeNH_2{\cdot}BH_3$, in the presence of Ir and Rh complexes.[4,5] This discovery not only represents an exciting addition to the growing field of inorganic polymers,[6] but offers a new route for the high yield preparation of boron nitride ceramics *via* the thermolysis of well-defined B–N macromolecules.[7]

In this paper we explore the use of *N*-heterocyclic carbenes (NHCs) for the dehydrogenation of various amine–borane substrates. Roesky and co-workers obtained evidence for the dehydrogenation of the parent adduct $H_3N{\cdot}BH_3$ in the presence of the carbene $I^tBu$ ($I^tBu$ = $[(HCN^tBu)_2C:]$), as the formation of the hydrogenated aminal $I^tBuH_2$ was detected; however the nature of the B–N products formed was not investigated.[8] If related chemistry can transpire with primary amine–borane adducts $RNH_2{\cdot}BH_3$ then this would represent a potential metal-free route to polyaminoboranes $[RNH–BH_2]_n$ (Scheme 1).



**Scheme 1** Metal-catalyzed dehydrocoupling of amine–boranes ([M] = transition metal catalyst) and potential *N*-heterocyclic carbene-mediated dehydrogenation chemistry.

## Results and discussion

### Dehydrogenation of primary alkyl amine–borane adducts

When the dehydrocoupling of amine–boranes is instigated by transition metal catalysts, further loss of $H_2$ from the B–N polymers (*e.g.* $[MeNH–BH_2]_n$) or oligomers can occur with

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prolonged reaction times and/or elevated temperatures to give the *N*-substituted borazines (*e.g.* $[MeNBH]_3$); this process is both thermodynamically and entropically favored.[4,9] Given our prior work with the *N*-heterocyclic carbene IPr (IPr = $[(HCNDipp)_2C:]$; Dipp = $2,6\text{-}^iPr_2C_6H_3$),[10] we explored this species as a dehydrogenation agent for the metal-free dehydrocoupling of various amine–borane adducts (Scheme 1).[11]

We began our studies by combining methylamine borane $MeNH_2{\cdot}BH_3$ with one equivalent of IPr in toluene. Analysis of the crude product mixture by $^1H$ NMR spectroscopy (in $C_6D_6$) revealed that the complete consumption of IPr had transpired and that the expected dihydroaminal $(HCNDipp)_2CH_2$-($IPrH_2$)[12] had formed, consistent with the carbene-induced dehydrogenation of $MeNH_2{\cdot}BH_3$. However, in addition to $IPrH_2$, a second carbene-containing product was detected by NMR spectroscopy suggesting that an alternative reaction pathway to what is outlined in Scheme 1 had occurred. $^{11}B$ NMR data corroborated this finding as two new closely-spaced broad resonances were detected at −14.0 and −14.7 ppm, while the anticipated polyaminoborane $[MeNH–BH_2]_n$ would have yielded a broad $^{11}B$ NMR resonance at −6.7 ppm.[4a] The $IPrH_2$ co-product was separated from the reaction mixture by extraction with hexanes to leave a single carbene-containing product as a white solid. Recrystallization of this material from a toluene–hexanes solution (10 : 1) at −35 °C afforded colorless crystals that were identified as the carbene-bound B–N–B complex, $IPr{\cdot}BH_2NH(Me)–BH_3$ (**1**) (Scheme 2; Fig. 1); relevant X-ray crystallographic data is listed in Table 1.

As shown in Fig. 1, $IPr{\cdot}BH_2NH(Me)–BH_3$ (**1**) adopts a *gauche* $C_{IPr}$–B–N–B arrangement [torsion angle = 62.49(16)°] with a slightly elongated terminal B(2)–N(3) distance [1.598(2) Å] in relation to the internal B(1)–N(3) linkage [1.5692(19) Å]. The terminal B–N bond in **1** is similar in length to the dative B–N interaction in $MeNH_2{\cdot}BH_3$ [1.5936(13) Å],[13a] while the internal B–N distance in **1** is identical within experimental error to the related internal B–N bond in MeNH–*B*$H_2$–*N*(Me)H–$BH_3$ [1.5730(19) Å].[13b] Interestingly, compound **1** can be formally regarded as a donor–acceptor adduct of an aminoborane $H_2BNMeH$ unit, that is itself derived from the dehydrogenation of $MeNH_2{\cdot}BH_3$.

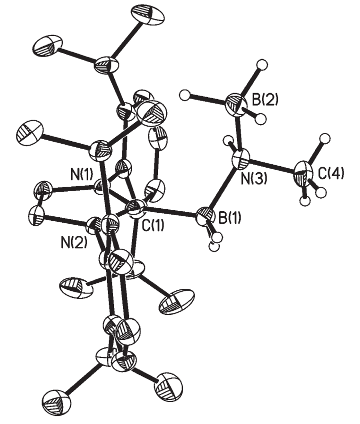
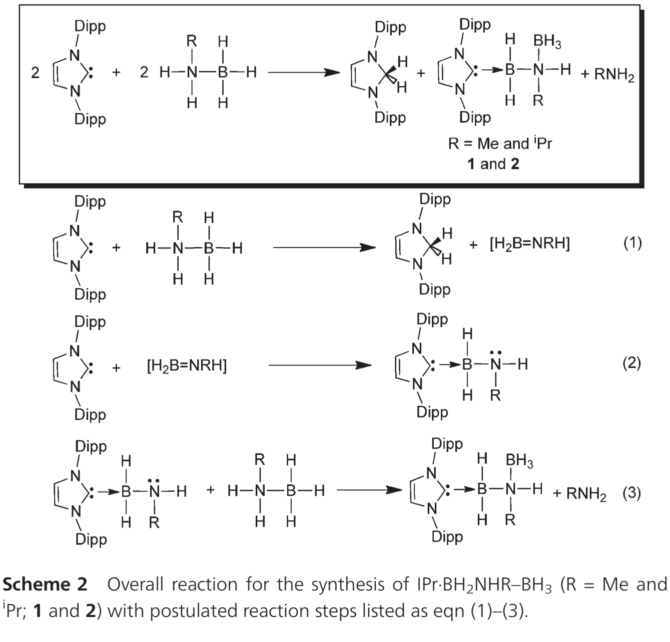


**Fig. 1** Thermal ellipsoid plot (30% probability level) of $IPr{\cdot}BH_2NH(Me)–BH_3$ (**1**). All hydrogen atoms on the IPr unit and toluene solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–B(1) 1.6128(18), B(1)–N(3) 1.5692(19), N(3)–B(2) 1.598(2), N(3)–C(4) 1.4825(18), N(3)–H 0.949(19), B–H 1.105(17) to 1.18(2); C(1)–B(1)–N(3) 113.52(10), B(1)–N(3)–C(4) 108.81(11), B(1)–N(3)–B(2) 116.07(12), B(2)–N(3)–C(4) 109.60(13); C(1)–B(1)–N(3)–B(2) torsion angle = 62.49(16).



**Scheme 2** Overall reaction for the synthesis of $IPr{\cdot}BH_2NHR–BH_3$ (R = Me and $^iPr$; **1** and **2**) with postulated reaction steps listed as eqn (1)–(3).

In order to explore the generality of the carbene-induced dehydrogenation chemistry described above, IPr was allowed to react with the more hindered primary amine–borane $^iPrNH_2{\cdot}BH_3$. As with the methylated analogue $MeNH_2{\cdot}BH_3$, formation of the expected hydrogenated product $IPrH_2$ was observed and the NMR spectra of the isolated co-product were consistent with the formation of the *N*-heterocyclic carbene complex $IPr{\cdot}BH_2N(^iPr)H–BH_3$ (**2**). Compound **2** gave similar spectral parameters as **1** and satisfactory combustion analyses (C, H and N) were obtained. Despite repeated attempts, crystals of **2** suitable for the production of high quality X-ray diffraction data could not be grown.

Scheme 2 outlines a potential reaction sequence for the formation of **1** and **2** from the interaction of $RNH_2{\cdot}BH_3$ with IPr (R = Me and $^iPr$). The overall reaction involves the generation of equimolar quantities of $IPrH_2$ and $IPr{\cdot}BH_2NH(R)–BH_3$ with the extrusion of free amine $RNH_2$. The presence of a 1 : 1 ratio between $IPrH_2$ and the carbene–borane products **1** and **2** was confirmed by $^1H$ NMR spectroscopic analysis of the reaction mixtures, while the formation of $^iPrNH_2$ was noted in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra when $^iPrNH_2{\cdot}BH_3$ and IPr were combined in a J. Young NMR tube (in $C_6D_6$). Thus far, we have been unable to detect or prepare the putative aminoborane intermediates $IPr{\cdot}BH_2NHR$ (R = Me and $^iPr$) outlined in Scheme 2.[14]

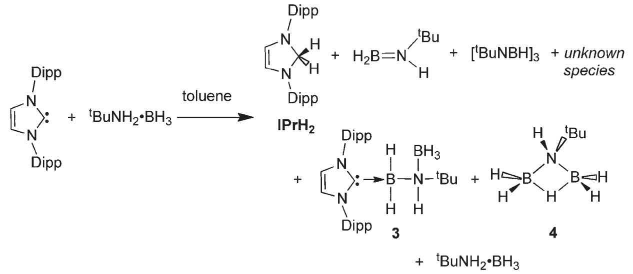
The *tert*-butylated adduct $^tBuNH_2{\cdot}BH_3$ was then allowed to react with IPr in toluene to verify the potential role of increased steric bulk on the chemistry described above.

**Table 1** Selected crystallographic data for compounds **1**, **3**, **6** and **7**

| | **1** | **3**·1.5THF | **6** | **7**·DCE |
|---|---|---|---|---|
| Empirical formula | $C_{35}H_{53}B_2N_3$ | $C_{37}H_{63}B_2N_3O_{1.5}$ | $C_{12}H_{22}BN$ | $C_{35}H_{36}BCl_2N$ |
| $M_r$ | 537.42 | 595.52 | 191.12 | 552.36 |
| $T$/K | 173(1) | 173(1) | 173(1) | 173(1) |
| $\lambda$/Å | 1.54178 [Cu Kα] | 1.54178 [Cu Kα] | 0.71073 [Mo Kα] | 1.54178 [Cu Kα] |
| Crystal system | Monoclinic | Monoclinic | Trigonal | Tetragonal |
| Space group | $P2_1/n$ | $P2_1/n$ | $R\bar{3}$ | $P42/mbc$ |
| $a$/Å | 14.5000(2) | 16.8935(5) | 15.4951(12) | 17.2578(2) |
| $b$/Å | 13.8866(2) | 13.6955(4) | | |
| $c$/Å | 17.5606(2) | 17.7459(5) | 27.816(2) | 20.4652(3) |
| $\beta$/° | 100.3528(6) | 107.4379(18) | | |
| $V$/Å$^3$ | 3478.36(8) | 3917.1(2) | 5783.9(8) | 6095.18(13) |
| $Z$ | 4 | 4 | 18 | 8 |
| $D_c$/g cm$^{-3}$ | 1.026 | 1.010 | 0.988 | 1.204 |
| $\mu$/mm$^{-1}$ | 0.435 | 0.452 | 0.055 | 2.082 |
| Crystal size/mm$^3$ | 0.35 × 0.24 × 0.22 | 0.55 × 0.32 × 0.10 | 0.49 × 0.32 × 0.13 | 0.27 × 0.19 × 0.14 |
| 2$\theta$ Range for data collection/° | 7.30–140.40 | 8.30–137.80 | 5.26–51.64 | 7.24–140.10 |
| Index ranges, $hkl$ | −17 to 17, −16 to 16, −21 to 21 | −20 to 20, −16 to 16, −21 to 21 | −18 to 18, −18 to 18, −33 to 33 | −21 to 21, −21 to 21, −20 to 22 |
| Reflections collected | 23 523 | 26 141 | 13 920 | 39 954 |
| Independent reflections | 6657 ($R_{int}$ = 0.0154) | 7069 ($R_{int}$ = 0.0358) | 2343 ($R_{int}$ = 0.0301) | 2989 ($R_{int}$ = 0.0180) |
| Range of transmission factors | 0.9123–0.8623 | 0.9554–0.7885 | 0.9928–0.9735 | 0.7536–0.6053 |
| Data/restraints/parameters | 6657/0/386 | 7069/0/349 | 2343/0/147 | 2898/0/206 |
| $R_1$ [$I > 2\sigma(I)$]$^a$ | 0.0488 | 0.0454 | 0.0406 | 0.0457 |
| w$R_2$ [all data]$^a$ | 0.1515 | 0.1344 | 0.1114 | 0.1351 |
| $\Delta\rho$/e Å$^{-3}$ | 0.368/−0.244 | 0.205/−0.182 | 0.140/−0.172 | 0.593/−0.755 |

$^a$ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Evidence for the dehydrogenation of $^t$BuNH$_2$·BH$_3$ was noted by NMR spectroscopy as IPrH$_2$ was identified[12] as the major species after the volatiles were removed *in vacuo*; in addition, *ca.* 10% of a new NHC-containing product was noted as a minor product in the $^1$H NMR spectrum. The latter species was identified as the expected B–N–B adduct IPr·BH$_2$N($^t$Bu)H–BH$_3$ (**3**) by comparison of the observed spectral parameters with those obtained from an independently prepared sample (*vide infra*). The formation of small quantities of **3** suggested that the chemistry outlined in Scheme 2 was transpiring to a significantly reduced degree for $^t$BuNH$_2$·BH$_3$ in comparison with the less hindered analogues, MeNH$_2$·BH$_3$ and $^i$PrNH$_2$·BH$_3$. When the reaction between $^t$BuNH$_2$·BH$_3$ and IPr was monitored *in situ* by $^{11}$B NMR spectroscopy, a number of previously known products could be detected (eqn (4)), including: the monomeric aminoborane [$^t$BuNH=BH$_2$] (35.2 ppm, t, $^1J_{BH}$ = 125 Hz, 7%),[15a] [$^t$BuNBH]$_3$ (25.9 ppm, d, $^1J_{BH}$ = 115 Hz, 30%),[15a,b] IPr·BH$_2$N($^t$Bu)H–BH$_3$ (−17.9, br, coincident *B*H$_2$ and *B*H$_3$ resonances, 12%, *vide infra*), $^t$BuNH$_2$·BH$_3$ (−21.9 ppm, q, $^1J_{BH}$ = 99 Hz, 35%), ($^t$BuNH)B$_2$H$_5$ (−25.8 ppm, m, 8%),[15c] and two unknown species [−8.3 ppm (br s, 5%) and a pentet resonance at −36.4 ppm ($^1J_{BH}$ = 82 Hz, 4%)[15d] consistent with a BH$_4^-$ anion]. From this product distribution, and the formation of IPrH$_2$, it appears that the dehydrogenation of $^t$BuNH$_2$·BH$_3$ occurred (eqn (1), Scheme 2). The presence of [$^t$BuNBH]$_3$ and $^t$BuNH$_2$·BH$_3$ is in line with a prior observation that [$^t$BuNH=BH$_2$] converts into [$^t$BuNBH]$_3$ and $^t$BuNH$_2$·BH$_3$ over time *via* transfer hydrogenation chemistry.[15a,16e] Thus it seems that further carbene coupling of IPr to transient [$^t$BuNH=BH$_2$] (eqn (2), Scheme 2) is largely suppressed due to the increased steric bulk and electron donating nature of the $^t$Bu group installed at nitrogen.



(4)

In order to confirm the formation of IPr·BH$_2$NH($^t$Bu)–BH$_3$ (**3**) as a minor species during the abovementioned reaction between $^t$BuNH$_2$·BH$_3$ and IPr, IPr·BH$_2$NH($^t$Bu)–BH$_3$ (**3**) was synthesized according to a related procedure used to generate IPr·BH$_2$NH$_2$–BH$_3$.[16f] Specifically, the *tert*-butylated complex **3** was obtained as a moisture-sensitive solid in a 61% yield *via* the ring-opening of ($^t$BuHN)B$_2$H$_5$ (**4**)[16f] with IPr (eqn (5)). Conclusive evidence for the formation of **3** was obtained by single-crystal X-ray diffraction (Fig. 2), which revealed the presence of a similar *gauche* disposed C$_{IPr}$–B–N–B chain in **3** as in its methylated congener **1**. As with compounds **1** and **2**, the proximal Dipp groups within the IPr ligand in **3** exhibit restricted rotation on the NMR timescale, as evidenced by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy. In addition, the central B*H*$_2$ hydrogen atoms in **3** exist in magnetically distinct environments ($\delta$ = 2.14 and 2.29 ppm; $^1$H NMR spectroscopy); a similar spectral effect was noted in MeNH$_2$·B*H*$_2$NMe(H)–BH$_3$.[13b]

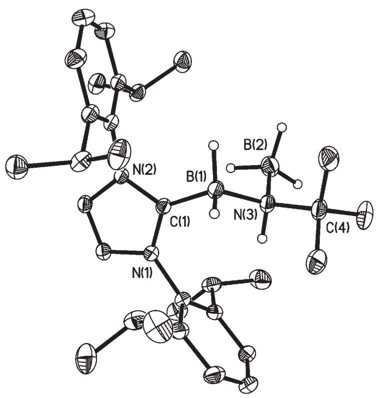
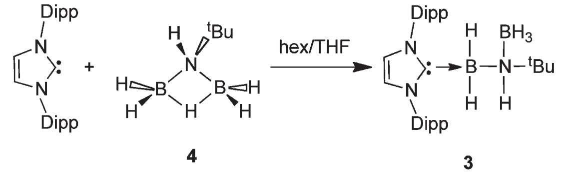


**Fig. 2** Thermal ellipsoid plot (30% probability level) of IPr·$BH_2NH(^tBu)$–$BH_3$ (**3**). All carbon-bound hydrogen atoms and THF solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–B(1) 1.6088(16), B(1)–N(3) 1.5929(15), N(3)–B(2) 1.6162(17), N(3)–C(4) 1.5276(14), B–H 1.110(16) to 1.125(13); C(1)–B(1)–N(3) 111.28(9), B(1)–N(3)–B(2) 110.21(9), B(1)–N(3)–C(4) 113.25(9); C(1)–B(1)–N(3)–B(2) torsion angle = 69.27(12).

The $^{11}B$ NMR spectrum of **3** contains a single broad peak at −17.9 ppm due to coincident $BH_2$ and $BH_3$ resonances (identified with the aid of $^1H\{^{11}B\}$ NMR experiments).



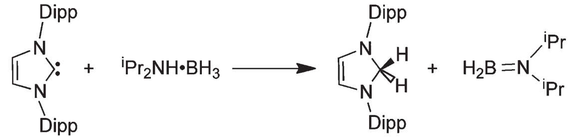
(5)

With IPr·$BH_2NH(^tBu)$–$BH_3$ (**3**) in hand, we explored the chemistry of this adduct with $^tBuNH_2$ to verify if **3** can be consumed in a reaction that is the reverse of eqn (3) in Scheme 2. However when **3** was combined with $^tBuNH_2$ in toluene, no reaction was observed at room temperature after three days; heating the reaction mixture to 60 °C for a further three days resulted in only a *ca.* 10% conversion of **3** into *tert*-butylborazine $[^tBuNBH]_3$ with no evidence of other products resulting from the dehydrogenation of $^tBuNH_2 \cdot BH_3$ (*e.g.* the products listed in eqn (4)). Thus the low yield of **3** obtained in the reaction of IPr with $^tBuNH_2 \cdot BH_3$ does not appear to be due to competing reactivity between **3** and any $^tBuNH_2$ generated.

The initial step of the reaction sequence in Scheme 2 involves the direct hydrogen transfer reaction between $RNH_2 \cdot BH_3$ and IPr to yield $IPrH_2$ and transient aminoboranes $H_2BNRH$ as products (eqn (1)). In the presence of added IPr, it is conceivable that the aminoborane adducts IPr·$BH_2NRH$ are formed due to the electron-deficient nature of the boron center in $H_2BNRH$ (eqn (2)).[14,17] For the cases where R = Me or $^i$Pr, once IPr·$BH_2NRH$ is formed, then the lone pair at nitrogen could participate in borane abstraction chemistry with unreacted $RNH_2 \cdot BH_3$ in solution to give the observed products **1** and **2** along with free amine $RNH_2$ (eqn (3)). When R = $^t$Bu, this overall process appears to be significantly slower enabling additional oligomerization, disproportionation and dehydrogenation chemistry to transpire with $[^tBuNH{=}BH_2]$ at the expense of forming IPr·$BH_2NH(^tBu)$–$BH_3$ (**3**).

## Dehydrogenation of the secondary amine–borane adduct $^iPr_2NH \cdot BH_3$

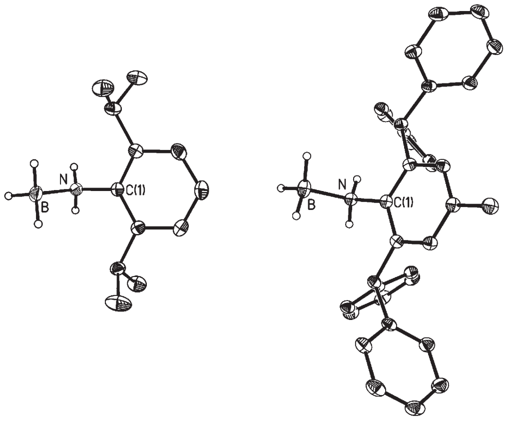
It is evident from the preceding section that the steric bulk at nitrogen plays an important role in dictating the outcome of the carbene-induced dehydrogenation chemistry. Interestingly, the reaction between the hindered secondary amine–borane $^iPr_2HN \cdot BH_3$ and IPr yields $IPrH_2$ and the known monomeric aminoborane $[^iPr_2N{=}BH_2]$[18] after 24 h in toluene at room temperature (eqn (6)). Due to the volatility of $[^iPr_2N{=}BH_2]$, $IPrH_2$ can be isolated from the reaction mixture in a 99% yield by simply removing $[^iPr_2N{=}BH_2]$ *in vacuo*. This synthesis represents a significant improvement over our prior route to $IPrH_2$, *via* the reaction between [IPrH]Cl and $Li[HBEt_3]$, which generates variable quantities of involatile IPr·$BEt_3$ by-product that is challenging to separate from $IPrH_2$.[12] The formation of $[^iPr_2N{=}BH_2]$ as the sole B–N product implies that this species is too weak of a Lewis acid to bind IPr. In support of this notion, attempts to form IPr·$BH_2N^iPr_2$ by the direct reaction of excess IPr with *in situ* generated $[^iPr_2N{=}BH_2]$ (prepared *via* the $Rh^I$ catalyzed dehydrogenation of $^iPr_2HN \cdot BH_3$ in refluxing toluene)[18] failed to give any observable reaction. This result suggests that if secondary amino–borane adducts IPr·$BH_2NR_2$ are formed in the abovementioned chemistry, they are likely unstable relative to dissociation into IPr and free aminoborane $[H_2B{=}NR_2]$. Notably, a formal donor–acceptor adduct of $H_2BNMe_2$, IPr·$BH_2NMe_2$–$BH_3$ (**5**), was recently synthesized,[16f] and highlights the requirement of a Lewis acidic ($BH_3$) group coordinated to nitrogen in order to intercept a stable carbene complex involving a secondary aminoborane $H_2BNR_2$ unit.



(6)

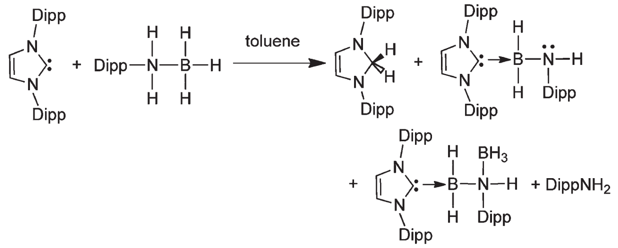
## Attempted dehydrocoupling of arylamine–boranes with an *N*-heterocyclic carbene

We also decided to investigate the potential dehydrogenation of electronically and sterically distinct hindered arylamine–borane adducts. To begin, the known adduct $DippNH_2 \cdot BH_3$[19] (**6**, Fig. 3) was combined with one equivalent of IPr in toluene at room temperature. Analysis of the resulting reaction mixture by $^1H$, $^{11}B$ and $^{13}C\{^1H\}$ NMR spectroscopy ($C_6D_6$) indicated the formation of the known species $IPrH_2$ (31%),[12] IPr·$BH_2NH$-Dipp (15%),[14] IPr·$BH_2NH(Dipp)$–$BH_3$ (22%)[14] and $DippNH_2$ (32%) as illustrated by eqn (7). Interestingly, this reaction produced identifiable products consistent with the reaction sequences (eqn (1)–(3)) outlined in Scheme 2. It is likely that a combination of the lower nucleophilicity of the nitrogen center in IPr·$BH_2NHDipp$ reduces the degree of $BH_3$ exchange between IPr·$BH_2NHDipp$ and $DippNH_2 \cdot BH_3$ (eqn (3)). In addition, the $BH_2NHDipp$ array is concurrently Lewis acidic enough to enable the isolation of the stable carbene–aminoborane adduct IPr·$BH_2NHDipp$ in the absence of exogenous $BH_3$ as a Lewis acid.



$H_3B{\bullet}NH_2(dipp)$ (**6**) $H_3B{\bullet}NH_2(Ar^*)$ (**7**)

**Fig. 3** Thermal ellipsoid plots (30% probability level) for $DippNH_2{\cdot}BH_3$ (**6**) and $Ar^*NH_2{\cdot}BH_3$ (**7**) with all carbon-bound hydrogen atoms and solvate molecules omitted for clarity. Selected bond lengths (Å) and angles (°): *Compound* **6**: C(1)–N 1.4633(14), B–N 1.6197(17), N–H 0.911(15) and 0.936(15), B–H 1.085(15) to 1.134(14); C(1)–N–B 116.31(10). *Compound* **7**: C(1)–N 1.465(2), B–N 1.641(3), N–H 0.929(19), B–H 1.13(2) and 1.20(3); C(1)–N–B 116.50(15); a crystallographic mirror plane bisects **7**.

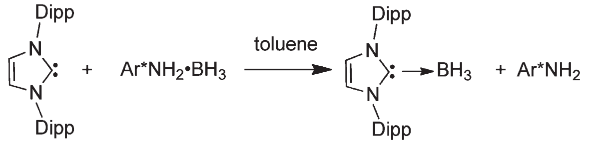


(7)

To explore if a sterically encumbered arylamine–borane adduct could participate in $BH_3$ exchange chemistry with IPr, we targeted the preparation of $Ar^*NH_2{\cdot}BH_3$ ($Ar^*$ = 2,6-$(Ph_2CH)_2$-4-$MeC_6H_2$). The synthesis of $Ar^*NH_2{\cdot}BH_3$ (**7**) was accomplished in quantitative yield from the treatment of $Ar^*NH_2$ [20] with a THF solution of $H_3B{\cdot}THF$. Compound **7** was obtained as an air-stable colorless solid that decomposes under $N_2$ with gas evolution at *ca.* 165 °C.[21] Crystals of **7** of suitable quality for single-crystal X-ray crystallography were obtained from a $ClCH_2CH_2Cl$–hexanes solution at −35 °C, and the refined structure is presented in Fig. 3 along with that of the less hindered Dipp analogue $DippNH_2{\cdot}BH_3$ (**6**).

The B–N bond length in $Ar^*NH_2{\cdot}BH_3$ (**7**) was found to be 1.641(3) Å, which is highly elongated when compared to the dative B–N interaction in $Me_2NH{\cdot}BH_3$ [1.5936(13) Å],[13a] and is longer than the B–N bond length in $DippNH_2{\cdot}BH_3$ [1.6197(17) Å]. Based on these metrical parameters it was anticipated that the B–N bond in **7** might be considerably weaker in relation to the B–N linkages found within alkylamine–borane adducts $R'NH_2{\cdot}BH_3$ (R′ = alkyl group).

In accordance with the presence of a weaker B–N interaction in $Ar^*NH_2{\cdot}BH_3$ (**7**), this species interacted with one equivalent of IPr to yield $IPr{\cdot}BH_3$ [22] and the hindered arylamine $Ar^*NH_2$ (eqn (8)), as determined by $^1H$, $^{11}B$ and $^{13}C\{^1H\}$ NMR spectroscopy. It has been observed that arylamine–boranes have weaker B–N bonds when compared with their alkyl amine–boranes.[21] This effect in conjunction with the significant steric bulk about nitrogen within the $Ar^*NH_2$ unit, likely facilitates the direct borane exchange reaction between $Ar^*NH_2{\cdot}BH_3$ and IPr in place of productive dehydrogenation chemistry.[23] We are currently exploring dehydrogenation chemistry as a route towards low coordinate B–N systems.[16f,24]



(8)

## Conclusions

The *N*-heterocyclic carbene IPr (IPr = [(HCNDipp)C:]; Dipp = 2,6-$^iPr_2C_6H_3$) is an effective dehydrogenation agent for *N*-alkylamine–boranes. Specifically, the primary amine–borane adducts $RNH_2{\cdot}BH_3$ (R = Me and $^iPr$) participate in clean chemistry with IPr to yield the hydrogenated aminal $IPrH_2$ and the carbene-capped B–N–B chains, $IPr{\cdot}BH_2NH(R)–BH_3$ as products; in the case of the more hindered adduct $^tBuNH_2{\cdot}BH_3$ a dramatic reduction in the amount of $IPr{\cdot}BH_2NH(R)–BH_3$ formed was noted. The secondary amine–borane adduct $^iPr_2NH{\cdot}BH_3$ interacts with IPr to give the dehydrogenated aminoborane $[^iPrN{=}BH_2]$ and $IPrH_2$. Due to a likely reduction in B–N bond strength, the arylamine–borane $Ar^*NH_2{\cdot}BH_3$ participates in a $BH_3$ exchange reaction with IPr, with no sign of productive dehydrogenation chemistry occurring. This study indicates that *N*-heterocyclic carbenes are effective stoichiometric dehydrogenation agents for amine–boranes, thus opening up new vistas of reactivity in terms of non-metal mediated dehydrogenation chemistry.[8,25]

## Experimental section

### General

All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[26] manufactured by Innovative Technology, Inc., degassed (freeze–pump–thaw method), and stored under an atmosphere of nitrogen prior to use. $^iPrNH_2$, $^tBuNH_2$, $^tBuNH_2{\cdot}BH_3$ and $H_3B{\cdot}THF$ were purchased from Sigma Aldrich; $^iPrNH_2$ and $^tBuNH_2$ were distilled prior to use, and all other chemicals were used as received. IPr,[27] $Ar^*NH_2$,[20] $^iPr_2NH{\cdot}BH_3$,[18] $^iPrNH_2{\cdot}BH_3$,[28] $(^tBuHN)B_2H_5$,[16f] and $DippNH_2{\cdot}BH_3$ [19] were prepared according to literature procedures. $^1H$, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with either Varian iNova 400 or VNMRS-500 spectrometers and referenced externally to $SiMe_4$ ($^1H$ and $^{13}C\{^1H\}$) and $Et_2O{\cdot}BF_3$ ($^{11}B$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded using

Nicolet IR100 FTIR as Nujol mulls between NaCl plates. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

### X-ray crystallography

Crystals of appropriate quality for X-ray diffraction studies were removed from a vial in a glovebox and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen.[29] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Cu or Mo Kα radiation, with the crystal cooled to −100 °C. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods[30] (SHELXD: **1**, **3**, **6** and **7**). Refinements were completed using the program SHELXL-97.[31] Where possible, boron and nitrogen bound hydrogen atoms were isotropically refined, otherwise were assigned positions based on the $sp^2$ or $sp^3$ hybridization geometries of their attached carbon, nitrogen or boron atoms and were given thermal parameters 20% greater than those of their parent atoms.

### Special refinement conditions

*Compound* **3**: Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent tetrahydrofuran oxygen or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure,[32] as implemented in *PLATON*.[33] A total solvent-accessible void volume of 1174.0 Å$^3$ with a total electron count of 244 (consistent with 6 molecules of solvent tetrahydrofuran, or 1.5 molecules per formula unit of the molecule of interest) was found in the unit cell.

### Synthetic procedures

**Synthesis of IPr·BH$_2$NH(CH$_3$)–BH$_3$ (1).** To a solution of IPr (0.242 g, 0.624 mmol) in toluene was added MeNH$_2$·BH$_3$ (0.028 g, 0.62 mmol) and the reaction mixture was stirred for 8 h. The volatiles were then removed *in vacuo* to yield a pale yellow powder, and the crude product was washed with 3 × 3 mL of hexanes to yield **1** as a colorless solid (0.113 g, 82%). Crystals suitable for X-ray crystallography were obtained by cooling a saturated solution of **1** in a 10 : 1 toluene–hexanes mixture to −35 °C. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.19–7.06 (m, 6H, Ar*H*), 6.46 (s, 2H, N–C*H*–), 3.05 (septet, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 2.93 (septet, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.18 (d, $^3J_{HH}$ = 6.0 Hz, 3H, –NH(C*H*$_3$)), 1.96 (s, 2H, –B*H*$_2$–, assignment made by selective $^1$H{$^{11}$B} decoupling), 1.94 (s, 3H, –B*H*$_3$, assignment made by selective $^1$H{$^{11}$B} decoupling), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.43 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$); the N*H* group was not located. $^{11}$B NMR (128 MHz, C$_6$D$_6$): $\delta$ = −14.0 (br, –*B*H$_2$–), −14.7 (br, –*B*H$_3$). $^{13}$C{$^1$H) NMR (100 MHz, C$_6$D$_6$): $\delta$ = 146.30 (Ar*C*), 146.28 Ar*C*), 133.8 (Ar*C*), 130.8 (Ar*C*), 129.3 (Ar*C*), 128.5 (Ar*C*), 125.6 (Ar*C*), 124.7 (Ar*C*), 124.2 (Ar*C*), 122.9 (–N–*C*H–), 43.3 (N(*C*H$_3$)$_2$), 28.9 ($^i$Pr), 28.8 ($^i$Pr), 26.0 ($^i$Pr), 25.9 ($^i$Pr), 23.0 ($^i$Pr), 22.9 ($^i$Pr). Anal. Calcd for C$_{28}$H$_{45}$N$_3$B$_2$: C, 75.52; H, 10.19; N, 9.44. Found: C, 75.50; H, 9.97; N, 9.27. Mp (°C): 181–182.

**Synthesis of IPr·BH$_2$NH($^i$Pr)–BH$_3$ (2).** To a solution of IPr (0.065 g, 0.17 mmol) in toluene was added $^i$PrNH$_2$·BH$_3$ (0.012 g, 0.17 mmol) and the reaction mixture was stirred for 8 h. The volatiles were then removed *in vacuo* to yield a pale yellow powder, and the crude product was washed with 3 × 3 mL of hexanes to yield **2** as a colorless solid that was recrystallized from THF at −35 °C (0.064 g, 80%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.17–7.05 (m, 6H, Ar*H*), 6.45 (s, 2H, N–C*H*–), 3.05 (septet, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.98 (m, 4H, C*H*(CH$_3$)$_2$), 2.20 (s, 2H, –B*H*$_2$–, assignment made by selective $^1$H{$^{11}$B} decoupling), 2.04 (s, 3H, –B*H*$_3$, assignment made by selective $^1$H{$^{11}$B} decoupling), 1.48 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.47 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, $^3J_{HH}$ = 6.5 Hz, 3H, –NCH(C*H*$_3$)$_2$), 0.99 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 0.79 (d, $^3J_{HH}$ = 6.5, 3H, –NCH(C*H*$_3$)$_2$); the N*H* group was not located. $^{11}$B NMR (128 MHz, C$_6$D$_6$): $\delta$ = −16.5 (br, –*B*H$_2$–), −17.9 (br, –*B*H$_3$). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$): $\delta$ = 146.5 (Ar*C*), 146.3 (Ar*C*), 133.9 (Ar*C*), 130.8 (Ar*C*), 124.8 (Ar*C*), 124.1 (Ar*C*), 122.6 (N–*C*H–), 53.5 (–N*C*H(CH$_3$)$_2$), 28.9 ($^i$Pr), 28.8 ($^i$Pr), 26.0 ($^i$Pr), 23.0 ($^i$Pr), 22.8 ($^i$Pr), 21.1 ($^i$Pr), 19.2 ($^i$Pr). Anal. Calcd for C$_{30}$H$_{49}$N$_3$B$_2$: C, 76.12; H, 10.43; N, 8.88. Found: C, 75.54; H, 10.52; N, 8.43. Mp (°C): 181–182.

**Reaction of $^t$BuNH$_2$·BH$_3$ with IPr.** To a solution of IPr (0.196 g, 0.505 mmol) in toluene was added $^t$BuNH$_2$·BH$_3$ (0.044 g, 0.51 mmol) and the resulting clear yellow solution was stirred for 8 h. Analysis of the reaction mixture by $^{11}$B NMR spectroscopy indicated the presence of the following species (with relative $^{11}$B integration values listed): $^{11}$B (128 MHz, toluene): $\delta$ = 35.2 ([$^t$BuNH=BH$_2$], t, $^1J_{BH}$ = 125 Hz, 7%), 25.9 ([$^t$BuNBH]$_3$, d, $^1J_{BH}$ = 115 Hz, 30%), −8.3 (unknown species, br s, 5%), −17.9 (IPr·*B*H$_2$NH($^t$Bu)–*B*H$_3$ (**3**), br s, coincident *B*H$_2$ and *B*H$_3$ resonances, 12%), −21.9 ($^t$BuNH$_2$·BH$_3$, quartet, $^1J_{BH}$ = 99 Hz, 35%), −25.8 ([($^t$BuNH)-B$_2$H$_5$], m, 8%), −36.4 (BH$_4^-$, pentet, $^1J_{BH}$ = 82 Hz, 4%). The volatiles were then removed from the reaction mixture to yield a pale yellow powder (0.169 g) that contained a mixture of IPrH$_2$ and **3** (90 : 10 ratio) by $^1$H NMR spectroscopy.

**Synthesis of IPr·BH$_2$NH($^t$Bu)–BH$_3$ (3).** To a solution of ($^t$BuHN)B$_2$H$_5$ (0.071 mmol in 5 mL of a 5 : 1 hexanes–THF mixture) was added IPr (0.277 g, 0.0698 mmol) and the mixture was heated at 60 °C for two days to yield a yellow solution. The solution was cooled to −35 °C for 24 h to yield **3** as colorless prisms (0.209 g, 61%). Crystals obtained from this method were suitable for X-ray crystallography. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ = 7.18 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 7.08 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.48 (s, 2H, N–C*H*–), 3.01 (m, 4H, C*H*(CH$_3$)$_2$), 2.29 (br s, 1H, –B*H*$_2$NH($^t$Bu)BH$_3$, assignment made by selective $^1$H{$^{11}$B} decoupling), 2.14 (br s, 1H, –B*H*$_2$NH($^t$Bu)-BH$_3$, assignment made by selective $^1$H{$^{11}$B} decoupling), 1.91 (br s, 3H, –BH$_2$NH($^t$Bu)B*H*$_3$, assignment made by selective $^1$H{$^{11}$B} decoupling), 1.46 (overlapping doublets, $^3J_{HH}$ = 6.5 Hz, 12H, –CH(C$H_3$)$_2$), 1.34 (br s, 1H, –N*H*($^t$Bu)), 1.08 (s, 9H, –C(C$H_3$)$_3$), 0.99 (d, $^3J_{HH}$ = 7.5 Hz, 6H, CH(C$H_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 7.5 Hz, 6H, CH(C$H_3$)$_2$). $^{11}$B NMR (160 MHz, $C_6D_6$): $\delta$ = −17.9 (br, $\Delta\nu_{1/2}$ = 168 Hz, –*B*H$_2$– and –*B*H$_3$ overlapping). $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): $\delta$ = 146.6 (Ar*C*), 146.4 (Ar*C*), 134.0 (Ar*C*), 130.7 (Ar*C*), 128.3 (Ar*C*), 124.9 (Ar*C*), 124.0 (Ar*C*), 122.5 (N–*C*H), 53.7 (*C*(CH$_3$)$_3$), 29.0 (CH(*C*H$_3$)$_2$), 28.7 (CH(*C*H$_3$)$_2$), 28.3 (CH(*C*H$_3$)$_2$), 26.0 (C(*C*H$_3$)$_3$), 22.9 (*C*H(CH$_3$)$_2$), 22.8 (*C*H(CH$_3$)$_2$). Anal. Calcd for $C_{31}H_{51}N_3B_2$: C, 76.39; H, 10.55; N, 8.62. Found: C, 75.25; H, 10.62; N, 8.50. Mp (°C): 110–111.

**Preparation of IPrH$_2$ from the reaction of $^i$Pr$_2$NH·BH$_3$ with IPr.** To a solution of IPr (0.143 g, 0.369 mmol) in toluene was added $^i$Pr$_2$NH·BH$_3$ (0.043 g, 0.37 mmol) and the resulting clear yellow solution was stirred for 8 h. The volatiles were removed *in vacuo* to yield a pale yellow powder that was redissolved in 5 mL of hexanes, and the solution was filtered. Removal of the solvent from the filtrate afforded spectroscopically pure IPrH$_2$ (pale yellow solid; 0.142 g, 99%) as determined by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy.[12]

**Synthesis of Ar*NH$_2$·BH$_3$ (Ar* = 2,6-(Ph$_2$CH)$_2$-4-MeC$_6$H$_2$) (7).** To a cold (−35 °C) solution of Ar*NH$_2$ (0.416 g, 0.946 mmol) in THF was added H$_3$B·THF (0.50 mL, 0.95 mmol, 1.0 M in THF), and the mixture was stirred for 4 h. The volatiles were removed *in vacuo* to yield **7** as a white solid (0.424 g, 98%). Crystals suitable for X-ray crystallography were obtained by cooling a saturated dichloroethane–hexanes (10 : 1) solution of **7** to −35 °C. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.08–6.94 (m, 20H, Ar–Ph*H*), 6.70 (s, 2H, Ar–C*H*(Ph)$_2$), 6.34 (s, 2H, Ar*H*), 4.66 (br s, 2H, Ar*N*H*$_2$), 2.88 (br s, 3H, Ar*NH$_2$B*H*$_3$, assignment made by broadband $^1$H{$^{11}$B} decoupling), 1.69 (s, 3H, –Ar*C*H*$_3$). $^{11}$B NMR (128 MHz, $C_6D_6$): $\delta$ = −16.1 (br, –*B*H$_3$). $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$): $\delta$ = 143.5 (Ar*C*), 142.1 (Ar*C*), 136.1 (Ar*C*), 136.0 (Ar*C*), 135.8 (Ar*C*), 130.4 (Ar*C*), 130.0 (Ar*C*), 129.1 (Ar*C*), 128.8 (Ar*C*), 127.5 (Ar*C*), 50.8 (*C*H(Ph)$_2$), 43.5 (*C*H(Ph)$_2$), 21.0 (Ar**C*H$_3$). Anal. Calcd for $C_{33}H_{32}NB$: C, 87.41; H, 7.11; N, 3.09. Found: C, 87.07; H, 7.10; N, 3.18. Mp (°C): 165 (decomp.).

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