

Reactions of Titanium Hydrazides with Silanes and Boranes: N–N Bond Cleavage and N Atom Functionalization

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S Supporting Information

ABSTRACT: Reaction of $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NNPh}_2)(\text{py})$ with $\text{Ph}(\text{R})\text{SiH}_2$ ($\text{R} = \text{H}, \text{Ph}$) or 9-BBN gave reductive cleavage of the $\text{N}_\alpha\text{--N}_\beta$ bond and formation of new silyl- or boryl-amido ligands. The corresponding reactions of $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^{\text{iPr}}\text{Pr})_2\}(\text{NNR}_2)$ ($\text{R} = \text{Me}$ or Ph) with HBPIn or 9-BBN gave borylhydrazido-hydride or borylimido products, respectively. N_α and N_β atom transfer and dehydrogenative coupling reactions are also reported.

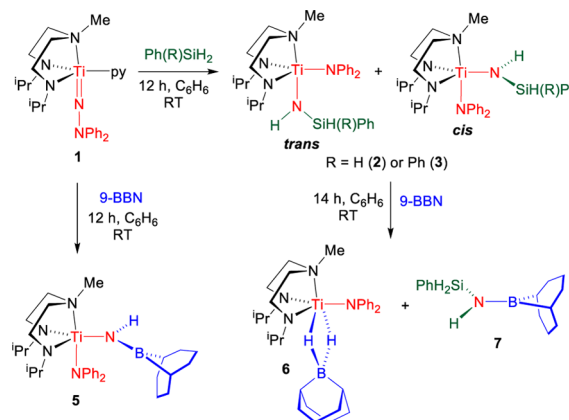
It has been shown over the last 5–8 years in particular (heralded by a preliminary communication in 1991¹) that group 4 hydrazides of the type $(\text{L})\text{M}=\text{NNR}_2$ ($\text{R} = \text{alkyl}, \text{aryl}$; $\text{L} = \text{ancillary ligand set}$) can undergo a variety of addition or insertion reactions of the $\text{Ti}=\text{N}_\alpha$ multiple bond with unsaturated substrates.^{1,2} While some aspects of the chemistry are reminiscent of that of the related and better-established group 4 imides $(\text{L})\text{M}=\text{NR}$,³ a distinctive aspect of group 4 hydrazido (and of the related alkoxyimides $(\text{L})\text{Ti}=\text{NOR}$ ⁴) is the typically facile reductive cleavage of the $\text{N}_\alpha\text{--N}_\beta$ bond that can also occur with oxidizable substrates such as CO ,¹ isocyanides,^{2d,1} and alkynes to form new N-element functional groups and/or organic products.^{2g,i,j}

Only one example of the reaction of Group 4 dialkylhydrazides with the Si–H bonds of silanes has been reported to date, namely the reversible 1,2-addition (without $\text{N}_\alpha\text{--N}_\beta$ bond cleavage) to the $\text{Ti}=\text{N}_\alpha$ multiple bond of $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^{\text{iPr}}\text{Pr})_2\}(\text{NNMe}_2)$.⁵ No reactions of hydrazido compounds with primary or secondary boranes are known (boranes without B–H bonds form Lewis adducts with the $\text{Ti}=\text{N}_\alpha$ atom of certain hydrazides²¹). There is precedent for Si–H addition to metal–heteroatom multiple bonds in general,^{3,6} but only one (very recently) structurally authenticated example of the 1,2-addition of a B–H bond to a transition metal imide.⁷

Of further relevance to the work described herein are the E–H bond activation, and in some cases subsequent N–N bond cleavage reactions, of early transition-metal-bound N_2 with Si–H⁸ or B–H⁹ bonds of silanes and boranes. These proceed via bimetallic intermediates in all instances. The subsequent N–N bond breaking reactions (forming silyl- or boryl-imido ligands) are sometimes accompanied by ancillary ligand degradation (especially in the case of the Group 5 borane reaction products) and are typically assisted (in Group 4) by addition of a reducing reagent such as CO.

We recently reported the unusual reactions of the diamide-amine-supported titanium hydrazide $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NNPh}_2)(\text{py})$ (**1**, Scheme 1) with certain alkynes in which the rather sterically

Scheme 1. Reactions of $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NNPh}_2)(\text{py})$ (**1**) with Phenyl Silanes and 9-BBN; Major Isomer of **5** and **6** shown



unencumbered ancillary ligand allows access to new types of intermediate and mechanism in hydrohydrazination catalysis.²ⁿ Here, we describe the reactions of this compound and a half-sandwich counterpart with selected silanes and boranes, leading to the reductive cleavage of the $\text{N}_\alpha\text{--N}_\beta$ bond and formation of silyl- and boryl-amido and imido species, along with N_α and N_β atom transfer and dehydrogenative coupling reactions.

Reaction of $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NNPh}_2)(\text{py})$ (**1**) with PhSiH_3 at rt gave quantitative conversion to $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})\{\text{N}(\text{H})\text{SiH}_2\text{Ph}\}(\text{NPh}_2)$ (**2**) which exists as two isomers, denoted *trans*-**2** and *cis*-**2**, in a 40:60% ratio (Scheme 1). When followed by ¹H NMR spectroscopy in toluene-*d*₈ from –78 °C to rt the reaction started to occur at ca. –10 °C, initially forming only *trans*-**2**, establishing this as the kinetic product. On warming to ca. 10 °C the *cis*-isomer started to appear, and after several hours at rt the thermodynamic equilibrium was established. Similar isomerizations have been noted elsewhere with this type of supporting ligand.²¹ Reaction with Ph_2SiH_2 gave an analogous product, namely $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})\{\text{N}(\text{H})\text{SiHPh}_2\}(\text{NPh}_2)$ (**3**), which likewise exists as a mixture of *trans* and *cis* isomers (50:50% ratio).

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The solid state structure of *trans*-**3** is shown in Figure 1 and reveals the complete cleavage of the N_α - N_β bond of **1** forming

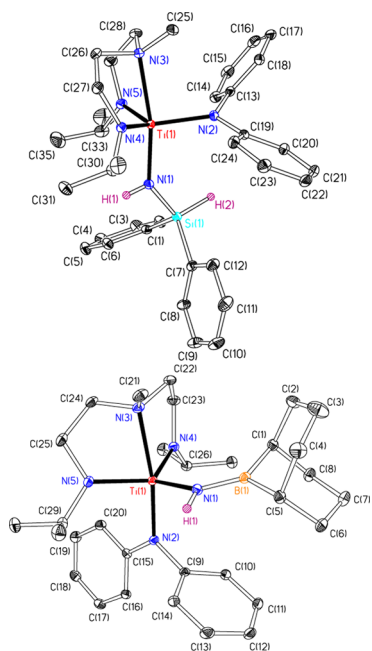


Figure 1. Displacement ellipsoid plots of *trans*- $\text{Ti}(\text{N}_2^{\text{iPrN}})\{\text{N}(\text{H})\text{-SiHPh}_2\}(\text{NPh}_2)$ (*trans*-**3**, top) and $\text{Ti}(\text{N}_2^{\text{iPrN}})\{\text{N}(\text{H})\text{BC}_8\text{H}_{14}\}(\text{NPh}_2)$ (**5**, bottom).

the new NPh_2 and $\text{N}(\text{H})\text{SiHPh}_2$ ligands (each having an N atom in a formal -3 oxidation state compared to -2 in **1**), positioned *cis* and *trans*, respectively, to the NMe moiety of N_2^{iPrN} . The NMR data for **2** and **3** are consistent with the solid state structure, in particular showing scalar coupling between the NH and SiH atoms of the $\text{N}(\text{H})\text{SiH}_x\text{Ph}_{3-x}$ ($x = 1$ or 2) ligands. These resonances are absent in the otherwise identical ^1H NMR spectrum of $\text{Ti}(\text{N}_2^{\text{iPrN}})\{\text{N}(\text{D})\text{SiD}_2\text{Ph}\}(\text{NPh}_2)$ (**2-d**₃) prepared using PhSiD_3 .

The formation of **2** and **3** from **1** represents the first reductive cleavage of a hydrazide (or related) $\text{N}-\text{N}$ bond by a silane at a single metal center, with net insertion of the N_α atom of **1** into a silane $\text{Si}-\text{H}$ bond. Further experiments and DFT calculations were carried out to probe the mechanism. Comparison of the reactions of **1** with PhSiH_3 or PhSiD_3 , by either initial rates (at -10°C) or a competition experiment between **1** and an excess of PhSiH_3 and PhSiD_3 (at rt) established a kinetic isotope effect in the range 1.34–1.41 for both types of experiment, comparable to

values found for $\text{Si}-\text{H}$ addition to $\text{Ti}=\text{S}^{6a}$ and $\text{Ti}=\text{O}^{6b}$ bonds. It was also found that the presence of an excess of pyridine decreased the rate of reaction (although competing unknown side reactions prevented a detailed analysis). Likewise, reaction of the DMAP analogue of **1**, $\text{Ti}(\text{N}_2^{\text{iPrN}})(\text{NNPh}_2)(\text{DMAP})$ (**4**, DMAP = 4-dimethylaminopyridine), with PhSiH_3 proceeded considerably more slowly to form **2**. Thus, both pyridine (or DMAP) loss and $\text{E}-\text{H}$ ($\text{E} = \text{Si}$ or B) bond cleavage are kinetically important to the rate-determining steps for the cleavage reaction.

DFT calculations found two related pathways for the formation of **2**, starting from different isomers of **1** (NNPh_2 , *trans* or *cis* to NMe). The lowest energy pathway (Figure 2) leads to the experimentally observed kinetic product *trans*-**2** which may then isomerize readily to the thermodynamic equilibrium mixture of *cis* and *trans* isomers.²¹ As is well-established for the reactions of many diamide-amine-supported imido and hydrazido analogues of **1**, the reaction proceeds via loss of pyridine to form four-coordinate **Int1**. The 1,2-addition of $\text{Si}-\text{H}$ to the $\text{Ti}=\text{N}_\alpha$ bond of **Int1** proceeds in a facile manner via intermediate **Int2** (relative $G = 13.3$ kcal mol⁻¹) to form the silylhydrazido-hydride species **Int3**. The barrier from this species, namely irreversible hydride transfer to N_α and highly exergonic reductive N_α - N_β bond cleavage, to give the final product at -58.7 kcal mol⁻¹ is readily accessible ($\Delta G^\ddagger = 17.3$ kcal mol⁻¹). The alternative pathway to that shown in Figure 2, starting from the *trans* isomer of **1** (Figure S1 of the Supporting Information (SI)), is almost identical, but the final transition state (analogous to **TS2**) has $\Delta G^\ddagger = 25.2$ kcal mol⁻¹ and is therefore uncompetitive. The highest points (**Int1**, **TS1**, and **TS2**) located on the lowest energy reaction pathway involve either pyridine loss from *cis*-**1** or $\text{Si}-\text{H}/\text{Ti}-\text{H}$ bond cleavage. Therefore, the computed mechanism is entirely consistent with the experimental observations presented above.

The unprecedented reactions of **1** with silanes prompted us to explore the corresponding reaction with boranes. Initial NMR tube-scale studies with pinacol borane gave rather complex spectra, possibly indicative of reaction at the $\text{Ti}-\text{N}_{\text{amide}}$ bonds of the N_2^{iPrN} ligand. Similar reaction outcomes were also found when halosilanes were used. However, as shown in Scheme 1, reaction of **1** with 1 equiv of 9-BBN dimer gave clean conversion to the borylamide $\text{Ti}(\text{N}_2^{\text{iPrN}})\{\text{N}(\text{H})\text{BC}_8\text{H}_{14}\}(\text{NPh}_2)$ (**5**) together with $\text{py}\cdot\text{HBC}_8\text{H}_{14}$. In solution **5** exists predominantly as the *cis* isomer (3:1 ratio of *cis/trans*) illustrated which was characterized by X-ray crystallography (Figure 1). Overall, the N_α atom of **1** has inserted into the $\text{B}-\text{H}$ bond of the borane with concomitant reductive cleavage of the N_α - N_β bond. This is also the first reaction of this type for a single metal center. DFT

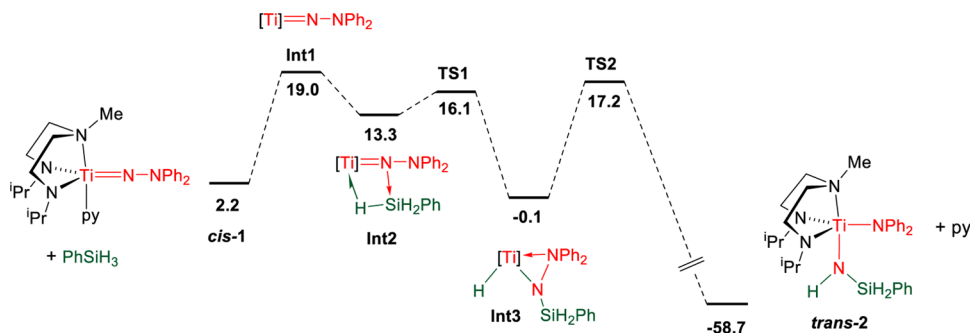


Figure 2. DFT mechanism for the reaction of *cis*-**1** with PhSiH_3 forming *trans*-**2** and py . Gibbs free energies (kcal mol⁻¹, $T = 298$ K) for minima, maxima, and transition states (labeled **TSx**) are shown in bold relative to *trans*-**1** and PhSiH_3 . $[\text{Ti}]$ represents $\text{Ti}(\text{N}_2^{\text{iPrN}})$.

calculations indicate an analogous mechanism to that for PhSiH_3 (see Figure S2). The key transition states for Si–H, B–H, and N–N bond breaking are shown in Figure S3.

The reductive transformations of a terminal (L)M=NR₂ functional group to the corresponding silylamido and borylamido ligands are unprecedented. We note, in this context, the recent report of Si–H and B–H bond addition to the terminal N atom of the vanadium(+5) nitride (^DiPPNacNac)V–(N)(NTol₂) forming V(+3) silyl- and boryl-amido products with net 2-electron reduction of the metal.¹⁰ These reactions (like their iridium¹¹ (Si–H) and osmium¹² (B–Ph) nitride addition precedents) are mechanistically distinct from those reported here which involve N–N bond cleavage with overall 1-electron reduction of the hydrazide N_{αβ} atoms as opposed to the metal center.

Compound **5** does not undergo reaction with further equivalents of 9-BBN. However, $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})\{\text{N}(\text{H})\text{SiH}_2\text{Ph}\}(\text{NPh}_2)$ (**2**) consumed 1 equiv of the borane dimer forming two new products, $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{NPh}_2)$ (**6**, confirmed by X-ray crystallography in Figure S4 of the SI) and the silylamino borane $\text{PhH}_2\text{SiN}(\text{H})\text{BC}_8\text{H}_{14}$ (**7**, Scheme 1). This reaction is quantitative when followed by ¹H NMR spectroscopy in C₆D₆, but the isolated yields are modest owing to the difficult separation of **6** and **7**. The reaction probably proceeds via a Ti–N/H–B exchange reaction forming a transient hydride $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{H})(\text{NPh}_2)$ and **7**, and then trapping of the transient hydride by borane forming a borohydride ligand. Overall the sequential reaction of **1**, first with PhSiH_3 and then 9-BBN, has resulted in total extrusion of N_α from the Ti=NNPh₂ linkage and formation of three different element–nitrogen bonds solely by reaction with Si–H and B–H bonds.

In principle, the new borylamide **5** could allow access to a borylimido analogue via elimination of Ph₂NH in the presence of a suitable donor. However, heating in the presence of bipy gave no apparent reaction, and specifically did not lead to the target six-coordinate $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N})(\text{NBC}_8\text{H}_{14})(\text{bipy})$. We speculated that a more sterically crowded/higher coordination number metal center might facilitate such a reaction and therefore turned to Cp*Ti{MeC(NⁱPr)₂}(NNR₂) (R = Me (**8a**) or Ph (**8b**)). Compound **8a** undergoes a number of small molecule activation reactions, including reversible 1,2-Si–H bond addition to $\text{Ti}=\text{N}_\alpha$ but without cleavage of the N_α–N_β bond.⁵

Reaction of **8a** with 1 equiv of pinacol borane (HBPIn) gave irreversible 1,2-addition of B–H to the $\text{Ti}=\text{N}_\alpha$ bond to form the borylhydrazido-hydride **9** (Scheme 2) which was isolated and crystallographically characterized (Figure 3). Compound **9** is analogous to the reaction intermediate **Int3** (Figure 2) shown by DFT to precede N_α–N_β bond cleavage en route to **2**. Although **9** is stable for weeks both in solution and the solid state at rt, upon heating to 70 °C in C₆D₆ decomposition occurs to a mixture of unidentified products. Compound **9** represents only the second fully authenticated B–H bond 1,2-addition product of a transition metal imide or hydrazide, the first being very recently reported for a rare terminal scandium imide.⁷

Reaction of **8a** with 0.5 equiv of 9-BBN dimer in C₆D₆ at rt gave ca. 50% conversion of the titanium complex and all of the borane to a 1:1 mixture of two boron-containing products as well as H₂ (as judged by a ¹H NMR singlet at 4.46 ppm) according to NMR spectroscopy. Scaling up the reaction with 1 equiv of 9-BBN dimer gave quantitative conversion of both starting materials to the borylimide $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^i\text{Pr})_2\}(\text{NBC}_8\text{H}_{14})$ (**10**) and the aminoborane $\text{Me}_2\text{NBC}_8\text{H}_{14}$ (**11a**)¹³ which was separated from **10** by careful vacuum sublimation. Compound **8b**

Scheme 2. Reactions of $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^i\text{Pr})_2\}(\text{NNR}_2)$ (R = Me (**8a**) or Ph (**8b**)) with Pinacol Borane and 9-BBN

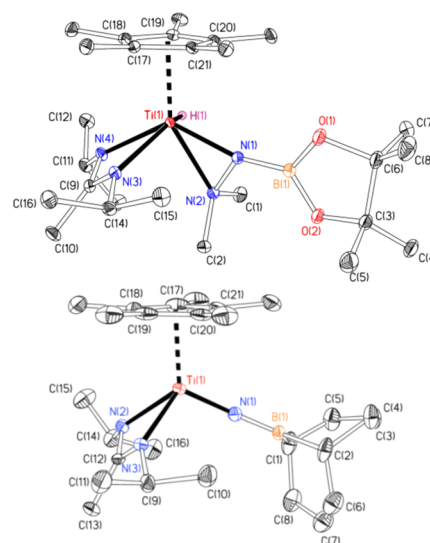
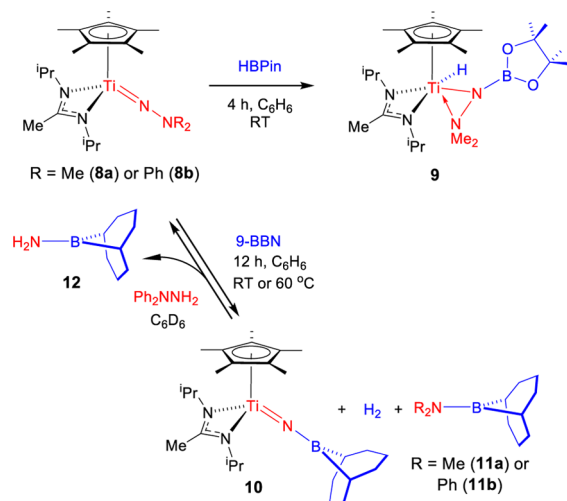


Figure 3. Displacement ellipsoid plot of $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^i\text{Pr})_2\}(\text{H})\{\text{N}(\text{NMe}_2)\text{BPIn}\}$ (**9**, top) and $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^i\text{Pr})_2\}(\text{NBC}_8\text{H}_{14})$ (**10**, bottom).

also reacted quantitatively with 9-BBN dimer in C₆D₆ at 60 °C to form **10** and Ph₂NBC₈H₁₄ (**11b**),¹⁴ together with H₂. It was not possible to fully separate **11b** from **10** on scale-up. The lower volatility of the aminoborane led to longer sublimation times and/or higher temperatures, giving thermal degradation of **10**.

The solid state structure of **10** is shown in Figure 3 and confirms the formation of the new borylimido ligand. Terminal transition metal borylimides are extremely rare, and there are no established synthetic routes.^{9a,15} Only one example has (very recently) been reported for group 4, this being Mindiola's $\text{Ti}(\text{NBET}_2)(\text{NTol}_2)\{\text{HC}(\text{C}^t\text{BuNDipp})_2\}$ prepared from the corresponding parent imide (Ti=NH functional group) and 2 equiv of NaHBET_3 , potentially via a nitrido intermediate.^{15c} The Ti(1)–N(1) bond length of 1.731(3) Å in **10** is identical within error to the Ti=NR distances in **8a** (1.723(2) Å) and **8b** (1.734(2) Å) and their xylimido analogue (1.738(2) Å) all of which have formal Ti≡N triple bonds ($\sigma^2\pi^4$). In addition, the N(1)–B(1) distance of 1.402(4) Å is typical¹⁶ of species of the type R₂N–BR'₂ which have significant N=B double bond

character via $N_{2p} \rightarrow B_{2p}$ π -donation. Molecular orbital and NBO analyses of the DFT structure of **10** support this interpretation (Figures S5 and S6 of the SI) by finding two Ti–N π -bonding interactions, one of which is significantly stabilized by delocalization into the otherwise vacant 2p AO of B(1) oriented perpendicular to the N(1)B(1)C(1)C(2) plane.

The conversion of a terminal hydrazide to a borylimide is a previously unknown reaction. Mechanistically, based on the other observations reported above, we propose that this proceeds first of all via 1,2-B–H addition to $Ti=N_{\alpha}$ to form an intermediate analogous to **9**. Hydride transfer to the N_{α} atom and reductive N_{α} – N_{β} bond cleavage would then form $Cp^*Ti\{MeC(N^iPr)_2\}\{N(H)BC_8H_{14}\}(NR_2)$ (**10_Int**), analogous to **5**. Subsequent 1,2-elimination of R_2NH from **10_Int** would form **10** and Ph_2NH (Ph_2NH does not react with **10**, consistent with this hypothesis). An independent control experiment confirmed that Ph_2NH and 9-BBN react quantitatively at 60 °C in the presence of **10** to form H_2 and **11b**.

Compounds **8a,b** are prepared from $Cp^*Ti\{MeC(N^iPr)_2\}(N^tBu)$ by protonolysis (tBuNH_2 elimination) using the appropriate hydrazine. In a similar manner, the reaction of **10** with 1 equiv of Ph_2NNH_2 in C_6D_6 quantitatively reformed **8b** and the aminoborane $H_2NBC_8H_{14}$ (**12**,¹⁷ Scheme 2; a corresponding reaction was observed for Me_2NNH_2 but was less clean). Overall, the reaction sequence in Scheme 2 converting **8b** into **10** and then back again may be viewed as the titanium-mediated reduction of Ph_2NNH_2 with 9-BBN dimer to form H_2 , $H_2NBC_8H_{14}$, and $Ph_2NBC_8H_{14}$. This is a new reaction of disubstituted hydrazines and boranes which usually undergo dehydrogenative N–B bond coupling without N–N bond cleavage.¹⁸

In summary we have reported the first examples of the Si–H or B–H induced reductive cleavage of a hydrazide N–N bond at a single metal center. These reactions can ultimately result in complete N_{α} or N_{β} atom transfer to substrate (i.e., formation of **7**, **11** and **12**) and encompasses the overall reduction of R_2NNH_2 with 9-BBN to the corresponding borylamines $R_2NBC_8H_{14}$ ($R' = Ph$ or H) and H_2 , a new type of dehydrogenative coupling reaction. Further work is ongoing to determine the mechanistic details, scope, and further potential of this and other borylimide-mediated dehydrogenative coupling reactions which are beyond the scope of this preliminary communication.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06627.

Synthetic procedures, characterizing data, further computational details (PDF)

Geometries of all the optimized structures as a single .xyz file (XYZ)

Crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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