Reactions of titanium hydrazides with silanes and boranes: N–N bond cleavage and N atom functionalization

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Supporting Information Placeholder

ABSTRACT: Reaction of $Ti(N_2{}^{iPr}N)(NNPh_2)(py)$ with $Ph(R)SiH_2$ (R = H, Ph) or 9-BBN gave reductive cleavage of the N_α–N_β bond and formation of new silyl- or boryl-amido ligands. The corresponding reactions of $Cp^*Ti\{MeC(N^iPr)_2\}(NNR_2)$ (R = 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.

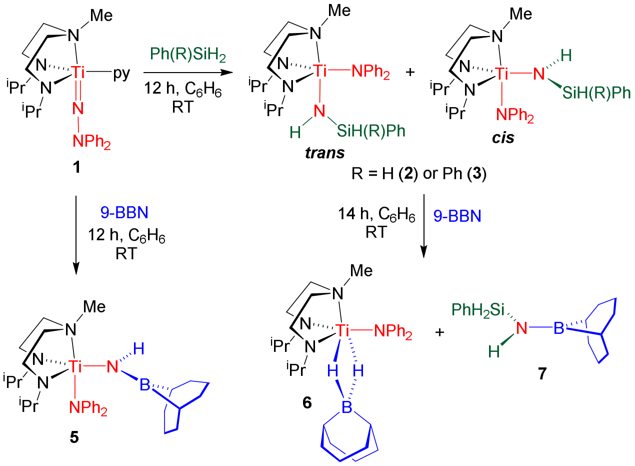
It has been shown over the last 5-8 years in particular (heralded by a preliminary communication in 1991[1]) that Group 4 hydrazides of the type $(L)M{=}NNR_2$ (R = alkyl, aryl; L = ancillary ligand set) can undergo a variety of addition or insertion reactions of the $Ti{=}N_\alpha$ multiple bond with unsaturated substrates.[1-2] While some aspects of the chemistry are reminiscent of that of the related and better-established Group 4 imides $(L)M{=}NR$,[3] a distinctive aspect of Group 4 hydrazido (and of the related alkoxyimides $(L)Ti{=}NOR$[4]) is the typically facile reductive cleavage of the N_α–N_β bond that can also occur with oxidizable substrates such as CO,[1] isocyanides[2d, 2l] and alkynes to form new N-element functional groups and/or organic products.[2g, 2i, 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 N_α–N_β bond cleavage) to the $Ti{=}N_\alpha$ multiple bond of $Cp^*Ti\{MeC(N^iPr)_2\}(NNMe_2)$.[5] No reactions of hydrazido compounds with primary or secondary boranes are known (boranes without B–H bonds form Lewis adducts with the $Ti{=}\underline{N}_\alpha$ atom of certain hydrazides[2l]). 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–H[8] or B–H[9] 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 $Ti(N_2{}^{iPr}N)(NNPh_2)(py)$ (**1**, Scheme 1) with certain alkynes in which the rather sterically unencumbered ancilliary ligand allows access to new types of intermediate and mechanism in hydrohydrazination catalysis.[2n] In this contribution we describe the reactions of this compound and a half-sandwich counterpart with selected silanes and boranes, leading to the reductive cleavage of the N_α–N_β bond and formation of silyl- and boryl-amido and imido species, along with N_α and N_β atom transfer and dehydrogenative coupling reactions.

Scheme 1. Reactions of $Ti(N_2{}^{iPr}N)(NNPh_2)(py)$ (1) with phenyl silanes and 9-BBN. Major isomer of 5 and 6 shown.



Reaction of $Ti(N_2{}^{iPr}N)(NNPh_2)(py)$ (**1**) with $PhSiH_3$ at RT (room temperature) gave quantitative conversion to $Ti(N_2{}^{iPr}N)\{N(H)SiH_2Ph\}(NPh_2)$ (**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.[2l] Reaction with Ph_2SiH_2 gave an analogous product, namely $Ti(N_2{}^{iPr}N)\{N(H)SiHPh_2\}(NPh_2)$ (**3**), which likewise exists as mixture of *trans* and *cis* isomers (50:50% ratio).

The solid state structure of ***trans*-3** is shown in Fig. 1 and reveals the complete cleavage of the N_α–N_β bond of **1** forming the new NPh_2 and $N(H)SiHPh_2$ 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 $N_2{}^{iPr}N$. The NMR data for **2** and **3** are consistent with the solid state structure, in particular showing scalar coupling between the N$\underline{H}$ and Si$\underline{H}$ atoms of the $N(H)SiH_xPh_{3-x}$ (x = 1 or 2) ligands. These resonances are absent in the otherwise identical ^{1}H NMR spectrum of $Ti(N_2{}^{iPr}N)\{N(D)SiD_2Ph\}(NPh_2)$ (**2-*d*$_3$**) prepared using $PhSiD_3$.

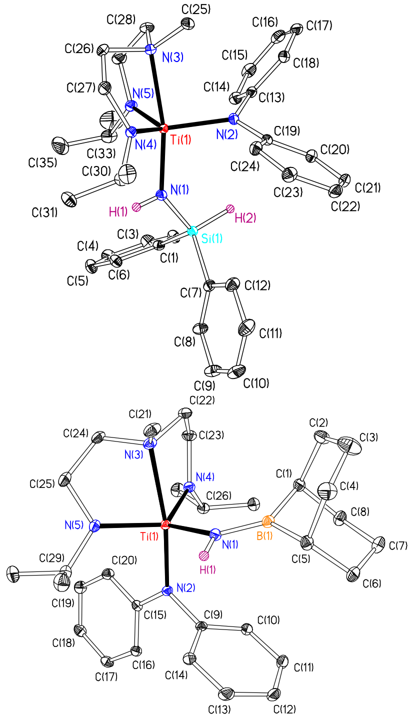


Figure 1. Displacement ellipsoid plots of *trans*-$Ti(N_2{}^{iPr}N)\{N(H)SiHPh_2\}(NPh_2)$ (***trans*-3**, top) and $Ti(N_2{}^{iPr}N)\{N(H)BC_8H_{14}\}(NPh_2)$ (**5**, bottom).

The formation of **2** and **3** from **1** represents the first reductive cleavage of a hydrazide (or related) N–N bond by a silane at a single metal center, with net insertion of the N_α atom of **1** into a silane Si–H bond. Further experiments and DFT calculations were carried out to probe the mechanism. Comparison of the reactions of **1** with $PhSiH_3$ or $PhSiD_3$, either by initial rates (at -10 °C) or by 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 Si–H addition to Ti=S[6a] and Ti=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**, $Ti(N_2{}^{iPr}N)(NNPh_2)(DMAP)$ (**4**, DMAP = 4-dimethylaminopyridine), with $PhSiH_3$ proceeded considerably more slowly to form **2**. Thus both pyridine (or DMAP) loss and E–H (E = 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 (Fig. 2) leads to the experimentally observed kinetic product ***trans*-2** which may then isomerise 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 Si–H to the Ti=N_α 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 Fig 2, starting from the *trans* isomer of **1** (Fig. S1 of the 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 Si-H /Ti-H bond cleavage. Therefore the computed mechanism is entirely consistent with the experimental observations presented above.

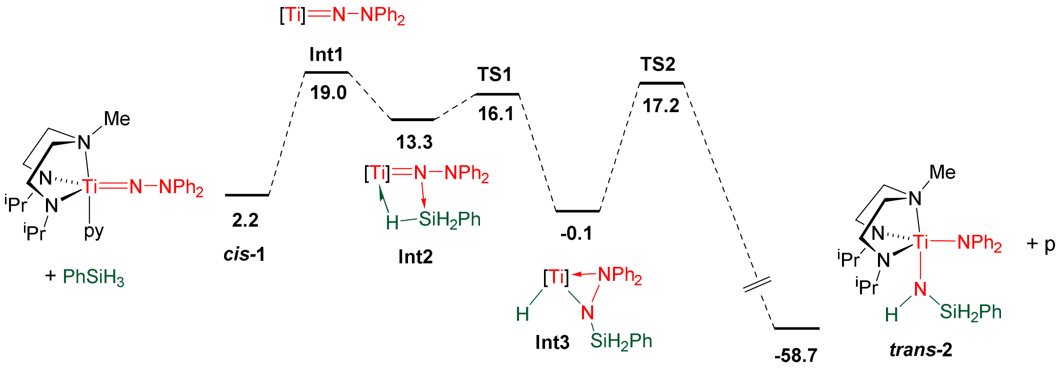


Figure 2. DFT mechanism for the reaction of ***cis*-1** with $PhSiH_3$ forming ***trans*-2** and py. Gibbs free energies (kcal mol^{-1}, T = 298 K) for minima, maxima and transition states (labeled **TSx**) are shown in bold relative to ***trans*-1** and $PhSiH_3$. [Ti] represents $Ti(N_2{}^{iPr}N)$.

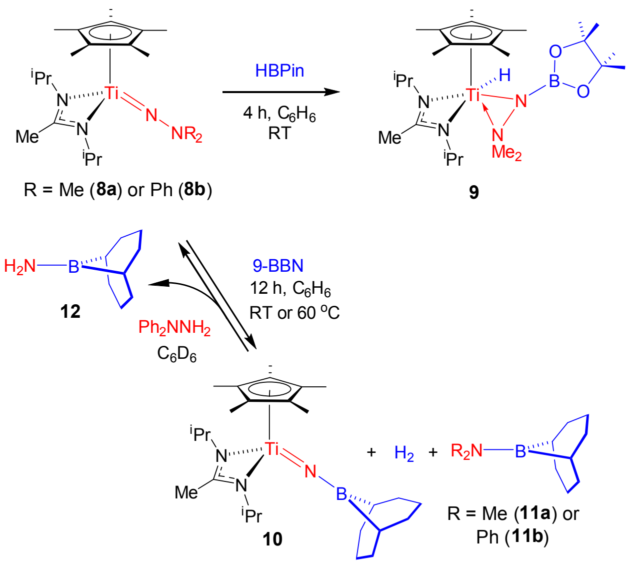
The unprecedented reactions of **1** with silanes prompted us to explore the corresponding reaction with boranes. Initial NMR tube-scale studies with pinacol borane gave rather complex spectra, possibly indicative of reaction at the $Ti\text{-}N_{amide}$ bonds of the $N_2{}^{iPr}N$ ligand. Similar reaction 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 $Ti(N_2{}^{iPr}N)\{N(H)BC_8H_{14}\}(NPh_2)$ (**5**) together with $py{\cdot}HBC_8H_{14}$. In solution **5** exists predominantly as the *cis* isomer (3:1 ratio of *cis*:*trans*) illustrated which was characterized by X-ray crystallography (Fig. 1). Overall, the N_α atom of **1** has inserted into the B–H bond of the borane with concommitant reductive cleavage of the N_α–N_β bond. This is also the first reaction of this type for a single metal center. DFT calculations indicate an analogous mechanism to that for $PhSiH_3$ (see Fig. S2). The key transition states for Si–H, B–H and N–N bond breaking are shown in Fig. S3.

The reductive transformations of a terminal $(L)M{=}NNR_2$ 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 $({}^{Dipp}NacNac)V(N)(NTol_2)$ forming V(+3) silyl- and boryl-amido products with net 2-electron reduction of the metal.[10] These reactions (like their iridium[11] (Si–H) and osmium[12] (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 $N_{\alpha,\beta}$ atoms as opposed to the metal center.

Compound **5** does not undergo reaction with further equivs of 9-BBN. However, $Ti(N_2{}^{iPr}N)\{N(H)SiH_2Ph\}(NPh_2)$ (**2**) consumed 1 equiv. of the borane dimer forming two new products, $Ti(N_2{}^{iPr}N)\{(\mu\text{-}H)_2BC_8H_{14}\}(NPh_2)$ (**6**, confirmed by X-ray crystallography in Fig. S4 of the SI) and the silylaminoborane $PhH_2SiN(H)BC_8H_{14}$ (**7**, Scheme 1). This reaction is quantitative when followed by ^1H NMR spectroscopy in C_6D_6 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 $Ti(N_2{}^{iPr}N)(H)(NPh_2)$ 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 $Ti{=}NNPh_2$ linkage and formation of 3 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 Ph_2NH in 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 $Ti(N_2{}^{iPr}N)(NBC_8H_{14})(bipy)$. We speculated that a more sterically crowded/higher coordination number metal center might facilitate such a reaction and therefore turned to $Cp^*Ti\{MeC(N^iPr)_2\}(NNR_2)$ (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 $Ti{=}N_\alpha$, but without cleavage of the N_α–N_β bond.[5]

Scheme 2. Reactions of $Cp^*Ti\{MeC(N^iPr)_2\}(NNR_2)$ (R = Me (8a) or Ph (8b)) with pinacol borane and 9-BBN.



Reaction of **8a** with 1 equiv. of pinacol borane (HBPin) gave irreversible 1,2-addition of B–H to the $Ti{=}N_\alpha$ bond to form the borylhydrazido-hydride **9** (Scheme 2) which was isolated and crystallographically characterized (Fig. 3). Compound **9** is analogous to the reaction intermediate **Int3** (Fig. 2) shown by DFT to preceed 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 C_6D_6 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 C_6D_6 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 H_2 (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 $Cp^*Ti\{MeC(N^iPr)_2\}(NBC_8H_{14})$ (**10**) and the aminoborane $Me_2NBC_8H_{14}$ (**11a**)[13] which was separated from **10** by careful vacuum sublimation. Compound **8b** also reacted quantitatively with 9-BBN dimer in C_6D_6 at 60 °C to form **10** and $Ph_2NBC_8H_{14}$ (**11b**),[14] together with H_2. 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**.

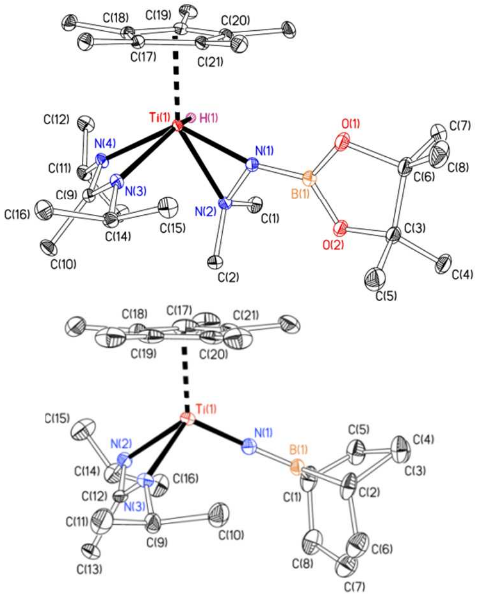
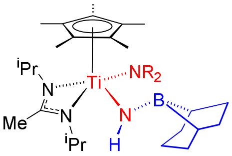


Figure 3. Displacement ellipsoid plot of $Cp^*Ti\{MeC(N^iPr)_2\}(H)\{N(NMe_2)BPin\}$ (**9**, top) and $Cp^*Ti\{MeC(N^iPr)_2\}(NBC_8H_{14})$ (**10**, bottom).

The solid state structure of **10** is shown in Fig. 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 $Ti(NBEt_2)(NTol_2)\{HC(C^tBuNDipp)_2\}$ prepared from the corresponding parent imide (Ti=NH functional group) and 2 equivs. $NaHBEt_3$, 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 xylylimido 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 typical[16] of species of the type R_2N–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 (Figs. 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_α 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**. -



10_int

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. Ph_2NNH_2 in C_6D_6 quantitatively re-formed **8b** and the aminoborane $H_2NB_8H_{14}$ (**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, $H_2NC_8H_{14}$ 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 $R_2NB_8H_{14}$ (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

Synthetic procedures, characterizing data, crystallographic data in CIF format, further computational details, and geometries of all the optimized structures as a single .xyz file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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