Terminal uranium(V)-nitride hydrogenations involving direct addition or Frustrated Lewis Pair mechanisms

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Despite their importance as mechanistic models for heterogeneous Haber Bosch ammonia synthesis from dinitrogen and dihydrogen, homogeneous molecular terminal metal-nitrides are notoriously unreactive towards dihydrogen, and only a few electron-rich, low-coordinate variants demonstrate any hydrogenolysis chemistry. Here, we report hydrogenolysis of a terminal uranium(V)-nitride under mild conditions even though it is electron-poor and not low-coordinate. Two divergent hydrogenolysis mechanisms are found; direct 1,2-dihydrogen addition across the uranium(V)-nitride then H-atom 1,1-migratory insertion to give a uranium (III)-amide, or with trimesitylborane a Frustrated Lewis Pair (FLP) route that produces a uranium(IV)-amide with sacrificial trimesitylborane radical anion. An isostructural uranium (VI)-nitride is inert to hydrogenolysis, suggesting the 5f¹ electron of the uranium(V)-nitride is not purely non-bonding. Further FLP reactivity between the uranium(IV)-amide, dihydrogen, and triphenylborane is suggested by the formation of ammonia-triphenylborane. A reactivity cycle for ammonia synthesis is demonstrated, and this work establishes a unique marriage of actinide and FLP chemistries.
Terminal metal-nitrides, M≡N, represent a key fundamental class of metal-ligand linkage in coordination chemistry. Although these M≡N triple bonds have been of elementary interest for over 170 years, only in relatively recent times has there been a concerted effort to study their reactivity. However, although a variety of reactivity patterns have emerged with metal-nitrides, the vast majority are remarkably unreactive because strong, often highly covalent M≡N triple bonds that result from high oxidation state metal ions—needed to bind to the hard, charge-rich nitride, N≡3—renders them inherently inert. One strategy to increase the reactivity of metal-nitrides is to utilise low oxidation state electron-rich metals to destabilise the M≡N triple bond, but by definition such metals are ill-matched to nitrides and so are difficult to prepare. Additionally, reactivity of metal-nitrides often involves ancillary ligands rather than the M≡N triple bond itself. Overcoming this challenge is difficult because there are very few metal-nitrides where the metal oxidation state or co-ligands can be varied within a homologous family to encourage M≡N triple bond reactivity.

Since there is an isoelectronic relationship between the M≡N and M=N triple bonds of metal-nitrides and dinitrogen, N≡N, there has thus been intense interest in the reactivity of metal-nitrides with H2 and indeed their use in the ammonia (NH3) synthesis, known as the Haber process. Although this has been well-studied, the vast majority of M≡N complexes are fundamentally mechanistically unreactive with respect to Haber Bosch chemistry where they are inherently inert. One solution to overcome this hydrogenolysis challenge may be to exploit frustrated Lewis Pair (FLP) chemistry, but so far this has been focussed on M–N2 complexes. Usually with mid- or late-transition metals, most metal-nitride hydrogenolyses involve sequential protonations, but bridging nitrides in poly-iron/titanium/zirconium complexes have been reported to react with H2 to give imido-hydride and NH3 products. Only three terminal metal-nitrides have been reported to undergo hydrogenolysis with H2. The isostuctural d4 ruthenium(IV)- and osmium(IV)-nitrides [M{N(CH2CH2PH3)2}2(N)] (M = Ru, Os) react with H2 using the ancillary ligand to shuttle H-atoms to evolve NH3 and the 5d6 iridium(III)-nitride [Ir{NC5H3-2,2'-C(Me)=N-2,6-Pr2-C6H3}2(N)] undergoes concerted reactivity with H2 to give [Ir{NC6H1-2,2'-C(Me)=N-2,6-Pr2-C6H3}2(NH3)]2. Thus, direct hydrogenolysis of a M≡N triple bond with H2 remains exceedingly rare, and involves reasonably electronic-rich (≥d4) metal complexes with low coordination numbers.

As part of our studies investigating actinide-ligand multiple bonding supported by triamidoamine ancillary ligands, we have reported two closely related terminal uranium-nitrides [UV(TrenTIPS)][K(B15C5)] (1) and [UV′(TrenTIPS)][N] (2) that, unusually, permit examination of the electronic structure and reactivity of the same isostuctural terminal nitride linkage with more than one metal oxidation state. Both react with the small molecules CO, CO2, and C2H2. However, only the protonolysis of 1 with H2O to give NH3 has been previously examined. The ability of 1 and 2 to react with H2 has remained an open question. Indeed, the study of molecular uranium-nitride reactivity remains in its infancy and only very recently the diuranium(IV)-nitride-cesium complex [Cs[U(OSi[OBU4]3)2]2(μ-N)] was reported to reversibly react with H2 to give the diuranium-imido-hydride complex [Cs[U(OSi[OBU4]3)2]2(μ-NH)(μ-H)]. Bridging nitrides tend to be more reactive than terminal ones, so whilst this nitride hydrogenolysis is enabled by the bridging nature of the nitride and polymetallic cooperativity effects, we wondered whether H2 activation by 1 or 2 might still be accessible, given prior protonation studies since this would realise the first terminal f-block-nitride hydrogenolyses. Further motivation to study this fundamental reaction stems from the fact that bridging and terminal uranium-nitride reactivity with H2 is implicated in Haber Bosch NH3 synthesis when uranium is used as the catalyst, and uranium-nitrides have been proposed as accident tolerant fuels (ATFs) for nuclear fission, but likely reactivity with H2 formed from radiolysis under extreme conditions or when stored as spent fuel remains poorly understood.

Here, we report that 2 does not react with H2 consistent with a strong U≡N triple bond that is inherently unreactive like many high oxidation state terminal metal-nitrides. However, in contrast 1 reacts with H2 under mild conditions despite the fact it can be considered to be a high oxidation state metal and not of a low coordination number nor electron-rich as a 5f metal ion. This hydrogenolysis reactivity is thus unprecedented in molecular metal-nitride chemistry, and further supports the emerging picture that suggests that the 5f-electron of 1 should not be considered as purely nonbonding. This study reveals two distinct H2 activation mechanisms. When the borane BMe3 (Mes = 2,4,6-trimethylphenyl) is present a FLP mechanism operates where two H2 heterolysis events and a borane reduction step sequentially combine to furnish a UIV-NH2 product, and this, to the best of our knowledge, is the first demonstration of the application of bona fide FLP reactivity to actinide chemistry. When the borane is absent, direct 1,2-addition of H2 across the U≡N triple bond to give a H−−U≡N−−H intermediate followed by H-atom migration produces a UIII-NH2 product that is easily oxidised to UIV-NH2. The direct addition is slower than the FLP-mediated mechanism, demonstrating the facilitating role of FLPs. We find evidence that treating the UIV-NH2 product with BPH3 and H2 produces further FLP hydrogenolysis reactivity, since H2NBPH3 has been detected in reaction mixtures, but this is reversible and produces products that react to give the starting materials. While currently of no practical use this demonstrates further potential for FLPs in this area. We demonstrate an azide to nitride to amide to ammonia reaction cycle, supported by overall hydrogenation involving hydrogenolysis and electrophilic quenching steps.

Results

Hydrogenolysis of the terminal uranium(V)-nitride bond. Since 2 was found to be unreactive or decomposed to a complex mixture of intractable products when exposed to boranes in the context of this study we examined the reactivity of 1. With or without H2, treatment of 1 in toluene with the strong Lewis acid B(C6F5)3 (BCF) results in decomposition as evidenced by 19F NMR spectra of reaction mixtures that show multiple fluorine resonances consonant with multiple C−F activation reactions, Fig. 1. Delanterious C−F bond activation reactivity is well documented for BCF, and so we examined the reactivity of 1 with the less Lewis acidic BPH3. However, when 1 is treated with BPH3 in toluene the adduct complex [U′(TrenTIPS)(NBPh3)][K(B15C5)] (3), which when compared to 1 and 2 is perhaps best formulated as a uranium(V)-imido-borate rather than a uranium(V)-nitrido-borate, is rapidly formed quantitatively and isolated in crystalline form in 66% yield, Fig. 1.

The retention of uranium(V) in 3 is supported by absorptions in the 5000–12,500 cm−1 region of its UV/Vis/NIR spectrum (Supplementary Fig. 1) that are characteristic of intraconfigurational 2F5/2 to 2F7/2 transitions of uranium(V) and by variable-temperature SQUID magnetometry, Fig. 2 and Supplementary

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Fig. 1 Synthesis of complexes 3–6. Treatment of 1 with the strong Lewis acid B(CsF_3)_3 results in decomposition, however the milder borane BPh_3 produces the capped species 3, which is inert with respect to reaction with H_2. Complex 1 does not react with the sterically encumbered BMes_3, but exposure of that mixture to H_2 produces the amide complex 4 with concomitant formation of the radical anion complex 5. Addition of H_2 to 1 produces the amide complex 6, and subsequent treatment with BMes_3 produces 4 and 5. Treating 4 with HCl produces NH_3. B15C5 = benzo-15-crown-5 ether. Mes = 2,4,6-trimethylphenyl.

Fig. 2. A powdered sample of 3 returns a magnetic moment of 2.23 μ_B at 300 K (1.96 μ_B by solution Evans method) that changes little until 30 K where it falls quickly to a moment of 1.38 μ_B at 2 K and this is consistent with the magnetic doublet character of 5² uranium(V). The U–N_mimoid bond length of 1.911(6) Å is consistent with the imidoborate formulation, for example distances of 1.916(4), 1.954(3), and 1.946(13) Å are found in [(Bu'ArN)_2U(V)(NBCF)][NBu^4(C_6F_5)] (Ar = 3,5-dimethylphenyl)²⁵, [U(V)(TrenTPP)(NSiMe_3)]²⁶, and [U(V)(TrenTPP)(NAd)] (Ad = 1-adamantyl)²⁷, respectively, and the B-N_mimoid distance of 1.581(9) Å compares well to the sum of the single bond covalent radii of B and N (1.56 Å)²⁸. The U–N_mimane distance of 2.737(5) Å is long, reflecting the dative nature of the amine donor and that it is trans to the strong imido donor, and the U–N_mimane distances (2.254(7)-2.312(6) Å) are slightly long for such distances²⁹, reflecting the formal anionic nature of the uranium component of 3.

Complex 3 does not react with H_2 (1 atm.), Fig. 1. Indeed, dissolving a mixture of 1 and BPh_3 under H_2 only generates 3, and so since BPh_3 has shut all reactivity down by strongly binding to the nitride of 1, but BCF is too reactive, we examined the use of BMes_3 (Mes = 2,4,6-trimethylphenyl). In principle, the ortho-methyls of the Mes groups of this borane block deactivating strong coordination of Lewis bases to the vacant p-orbital of boron whilst retaining a Lewis acidic boron centre.

To provide a reactivity control experiment, we stirred a 1:1 mixture of 1:BMes_3 in toluene under an atmosphere of N_2 and find no evidence for any adduct formation, Fig. 1, with only free BMes_3 being observed as evidenced by a resonance at 76.8 ppm in the ²H NMR spectrum of the reaction mixture. Repeating this reaction, but under H_2 (1 atm.), over two days at 298 K results in complete consumption of starting materials with deposition of a dark blue solid. The brown supernatant was removed and found by NMR spectroscopy to contain the known uranium(IV)-amide [U(V)(TrenTPP)(NH_2)] (4) in 67% yield, Fig. 1, as evidenced by a resonance at 107 ppm in its ²H NMR spectrum that corresponds to the amide protons. A control experiment, stirring 1 in toluene over two weeks, also produces 4 from trace, adventitious sources of H^+, though in far lower proportions, so to prove that the source of H-atoms in 4 originates from H_2 and not adventitious H^+³⁸, the reaction was repeated under D_2 (1 atm., 99.8% atom D). Interestingly, whilst [U(V)(TrenTPP)(ND_2)] (4′, ¹H δ 107.5 ppm) is formed, confirming that hydrogenolysis by H_2/D_2 does indeed occur, it is always accompanied by 4 and [U(V)(TrenTPP)(NHD)] (4″, ¹H δ 106.8 ppm, ²H δ 75.9 ppm not resolved). This reveals that H/D exchange occurs over time, so to determine the source of this exchange we studied the reaction of I and BMes_3 with all combinations of H_2/D_2 with H_6-/D_6-benzene and H_8-/D_8-toluene (see Supplementary Methods). We find that when H_2 is used only 4 is ever detected, but when D_2 is used 4, 4′, and 4″ all form (av. 12, 24, and 64% respectively) irrespective of whether the solvent is deuterated or not which rules out arene solvents as the H-source. However, when using C_6H_6 as solvent for the reaction of I with BMes_3 and D_2 a weak resonance is observed at −5.2 ppm in the ²H NMR spectrum (cf −5.35 and −5.87 ppm for iso-propyl methine and...
H2 can be a two-electron reducing agent and uranium(V) is void of D-atoms. TrenTIPS is void of D-atoms. We therefore suggest that the H-source is the TrenTIPS Pri groups since they have precedent for forming cyclometallates57, a reversible amide/imido-cyclometallate + H2 equilibrium can be envisaged since it has been previously shown that uranium-Tren-cyclometallates can react reversibly with H2/D259, and this would also account for the absence of D-scrambling into 4 since TrenTIPS is void of D-atoms.

The dark blue solid was isolated and after work-up obtained as methyl protons, respectively, in the 1H NMR spectrum of 4. We therefore surmise that the H-source is the TrenTIPS Pri groups since they have precedent for forming cyclometallates57, a reversible amide/imido-cyclometallate + H2 equilibrium can be envisaged since it has been previously shown that uranium-Tren-cyclometallates can react reversibly with H2/D259, and this would also account for the absence of D-scrambling into 4 since TrenTIPS is void of D-atoms.

The dark blue solid was isolated and after work-up obtained as dark blue crystals, identified as the radical species [K(B15C5)2][BMes3]5 in 69% yield. This compound has been structurally characterised by single crystal diffraction, see Supplementary Fig. 4. Compound 5 is very similar to [Li(12-crown-4)][BMes3]60 that contains the same radical anion component, and the EPR data of 5 (g = 2.003, A(11B) = 9.44 G, A(10B) = 2.7 G, A(1H) = 1.2–1.4 G, Fig. 4a, confirm the formation of the BMes3− radical anion formulation. The UV/Vis/NIR spectrum of 5 exhibits an intense, (ε = ~8000 M−1 cm−1) broad absorption centred at ~12,800 cm−1, which largely accounts for its dark blue colour, see Supplementary Fig. 5.

Since 4 does not form an adduct with BMes3, but the introduction of H2 leads to hydrogenolysis to give the amide 4, we surmised that the I/BMesor mixture may constitute a Frustrated Lewis Pair (FLP) system that is evidently capable of activating H2, which is confirmed computationally (see below). However, since H2 can be a two-electron reducing agent and uranium(V) is normally quite oxidising, we hypothesised that the BMesor may not actually be required. In effect, when 4 is produced it is essentially at the expense of the sacrificial one-electron reduction of BMesor to BMesor+, which would formally invoke a uranium(III)-amide precursor that would be nicely in-line with a H2-uranium(V) two-electron redox couple. In order to test whether the FLP aspect of this hydrogenolysis chemistry is vital to effecting dihydrogen activation a toluene solution of 1 under H2 (1 atm.) was stirred without BMesor. Over seven days 1 is consumed with concomitant precipitation of a gray solid identified as the uranium(III)-amide [UⅢ(TrenTIPS)(NH2)][K(B15C5)2] (6) (45% yield), Fig. 1. The hydrogenolysis reaction is now slower than when BMesor is present, but the reaction is best conducted at 288 and not 298 K, which may also retard the rate of reactivity. When the reaction is alternatively conducted under D2 (1 atm.), a mix of 6, [UⅢ(TrenTIPS)(NHD)][K(B15C5)2] (6′) and [UⅢ(TrenTIPS)(ND2)][K(B15C5)2] (6″) are isolated (66% yield by uranium content) analogously to 4/4′/4″, again indicating H/D exchange but confirming the H-atoms of the amide unit in 6 originate from gaseous H2. Consistent with these observations, we find that 1 also reacts with 9,10-dihydroanthracene (pKa 31 in DMSO, cf 34±4 for H2 in DMSO)61 to produce an insoluble precipitate and 4 in solution. From this solution we isolated a small crop of red crystals formulated by 1H NMR spectroscopy and X-ray
In order to experimentally link 6–4 we treated 6 with one equivalent of BMe₃ resulting in immediate reduction of BMe₃ to give a 1:1 mixture of 4 and 5, Fig. 1, which is in-line with the reducing nature of 6 as evidenced by ready formation of 4 in supernatant reaction mixtures. These reactions show that although the FLP aspect of the reaction of H₂ with 1 certainly facilitates and accelerates the hydrogenolysis of the nitrile linkage, it is not essential, and the terminal uranium(V)-nitrile linkage is reactive enough in its own right to be hydrogenated with H₂ to give a uranium(III)-amide, and this is confirmed computationally (see below).

Ammonia synthesis via strong acid. After the hydrogenolysis reactions that produce 4 and 6 we vacuum transferred volatile materials onto hydrochloric acid, but in each case no more than a 5% yield of NH₃, as its conjugate acid NH₄⁺, was detected by standard methods. This suggests that although the U⁵⁺=N-nitrile linkage reacts with one equivalent of H₂ to give U⁴⁺/IV-NH₂, further reaction of the latter linkages with H₂ does not occur. Direct treatment of 4/4’/6/6’ with 0.01 M HCl in THF/Et₂O to differentiate the D⁺ as from D₂ and not D⁺ acid, vacuum transfer onto a 2 M HCl in Et₂O acid trap, then assay, revealed a mixture of NH₄H⁺ (2 Δδ 7.12 ppm) and NH₄⁺ (1H Δδ 7.28 ppm, 1:1 triplet, JNH = 51 Hz) by ¹H NMR spectroscopy. Addition of H₂O results in full D/H exchange to give NH₄⁺ as the sole ammonium species in 52% yield. Analogously, 6/6’ produces NH₄⁺ in 46% yield, and if the HCl acid steps are replaced with analogous DCl reagents then NH₃D⁺ is first obtained and when this is converted to NH₄⁺ a similar yield of 48% is obtained showing the internal consistency of this approach, Supplementary Figs. 9, 10. Under the action of strong acid the main by-product is Tren⁴⁺/BPh₃ from over-protonation, but up to 31% [U⁴⁺(Tren⁴⁺)(CD)] (7) could be observed by ¹H NMR spectroscopy as would be expected from the reaction of 4 with HCl.

Reversible ammonia-borane formation. Since H₂ does not react with 4 or 6 on their own, we examined whether addition of a borane would facilitate a second hydrogenolysis step; utilising BCF or BMe₃ with H₂ results in no reaction and/or formation of unknown, intractable products. We find, however, that 4 reacts with BPh₃ to form the uranium(IV)-amide-borane adduct [U⁴⁺(Tren⁴⁺)(NH₂BPh₃)] (8), Fig. 6, as evident by its solid-state structure, Fig. 7. The salient feature of the structure of 8 is that although the Tren--Uamide and U--Amide distances of 2.645(5) and 2.221(5)-2.246(5) Å are unexceptional for Tren-uranium(IV) distances ⁵⁷, the U--NH₂ and U--Amide distance of 2.578(5) Å is very long ⁵⁴, suggesting that coordination of BPh₃ has severely weakened the U--NH₂ linkage. However, there is clearly a balance of steric clashing in this region of the molecule since the B-nitride distance of 1.637(9) Å is ~0.06 Å longer than the analogous distance in 3 and ~0.08 Å longer than the sum of the covalent single bond radii of B and N (1.56 Å) ⁵⁶. Variable-temperature SQUID magnetometry on a powdered sample of 8, Fig 2 and Supplementary Fig. 11, confirms the uranium(IV) formulation of this complex. Specifically, the magnetic moment of 8 at 300 K is 3.17 μB and this decreases smoothly to a value of 0.89 μB at 2 K and is tending to zero ⁵²–⁵⁴. This is characteristic of uranium(IV) which is a magnetic singlet at low temperature but that exhibits a small contribution from temperature independent paramagnetism to give a nonzero magnetic moment.

The ¹¹B NMR spectrum of 8 dissolved in C₅D₅ or C₆D₅CD₃ at 293 K exhibits resonances at 67.5 and ~3.2 ppm, corresponding to free BPh₃ and H₂NBPh₃, respectively, as confirmed by comparison to authentic samples. The implication, consistent with the long U--Amide and B--Amide distances in 8, is that 8 is in
equilibrium with 4 and free BPh3 in solution by B–N bond cleavage, but also that the long U–N amide bond is weakened increasing the basicity of this amide resulting in its rupture, C–H bond activation, and N–H bond formation to concomitantly form H3NBPh3 and the uranium(IV)-cyclometallate complex [UIV\(\text{N(CH}_2\text{CH}_2\text{NSiPr}_3\text{)}\text{2}(\text{CH}_2\text{CH}_2\text{NSiPr}_3\text{CH}(_2\text{CH}_2\text{)}\text{)})\] (9). Indeed, trace resonances that match reported data65 for 9 could be observed. A variable-temperature \(^1\text{H}\) and \(^{11}\text{B}\)[\(^1\text{H}\)] NMR study (Supplementary Figs. 12, 13) reveals that at 293 K the dominant products are 4 and free BPh3, but as the temperature is lowered to 253 and then 233 K resonances attributable to 8 grow in as 4 diminishes such that at 253 K the ratio of 4:8 is ~2:1 and at 233 K this ratio is ~2:3. However, when 9 is treated with H3NBPh3, the formation of 4 and BPh3 are observed by \(^1\text{H}\) NMR spectroscopy. This suggests facile, unspecific reversible reactivity but also hints at FLP-type reactivity, so we dissolved a 1:1 mixture of 4 and BPh3 under H2 (1 atm.), but again find only trace quantities of H3NBPh3. If 8 reacts with H2 to form H3NBPh3 and [UIV(TrenTIPS)(H)] (10) the latter would be anticipated to eliminate H2 to give cyclometallate 9. Indeed, treating [UIV(TrenTIPS)(THF)][BPh3] with NaNBPh3 to nominally produce [UIV(TrenTIPS)(HBPh3)] gives H2, BPh3, and 9 in addition to the anticipated NaBPh4 by-product. The reaction cycle in Fig. 6 can thus be proposed where 4 reacts with BPh3 and H2 to give, possibly via 8, H3NBPh3 and 10, the latter of which extrudes H2 to give 9. Since it is known that 9 reacts with H3NBPh3 to give 8 and/or 4 and free BPh3 then a cycle is most likely established where reactivity is occurring but no discernable products can be isolated since the products react with one another to give the starting materials. Though of little use currently, the formation of H3NBPh3 suggests that it may be possible to extract out and trap the NH3, though so far this system has resisted attempts to do so.

Closing an ammonia synthesis reaction cycle. Having effected hydrogenolysis of H2 but found that further reaction with H2 either does not occur or seems to occur in a borane-cycle with no discernable products, we sought to close a reaction cycle utilising an electrophile. Accordingly, treatment of 4, either prepared directly from 1/H2/BMes3 or stepwise via 6, with Me3SiCl produces 7 and Me3SiNH2 that can be quantitatively converted to NH3 in the form of ammonium salts. Under nonoptimised conditions an equivalent NH3 yield of 53% was achieved. Thus, a reaction cycle for azide to nitride to amide to ammonia by hydrogenation overall is demonstrated at uranium using hydrogenolysis of H2 followed by an electrophilic elimination and acid quench, Fig. 8.

Computational reaction mechanism profiles. In order to understand the reactions that produce 4/5 and 6, DFT calculations (B3PW91) corrected for dispersion- and solvent-effects were carried out to determine possible reaction pathways for the reaction of complex 1 with H2 in the presence or absence of BMes3, Supplementary Tables 1–25. We also computed the reaction profile for the hypothetical reaction of 2 with H2 (Supplementary Fig. 14), which confirms the experimental situation of no observable reactivity of 2 with H2. In the absence of BMes3, Fig. 9, H2 reacts with 1 in a σ-bond metathesis fashion. The associated barrier is relatively low (14.4 kcal mol\(^{-1}\)). At the transition state (B), the H–H bond is strongly elongated (1.02 Å) and the N–H bond is not yet formed (1.35 Å). The U–N\(_{\mathrm{nitride}}\) bond is 1.84 Å and the U–H distance is long (2.20 Å). The N–H–H angle is 146.3°, which is quite acute for a metathesis reaction. The NPA charges at the transition state (TS) [U, +1.12; N, −0.84; H, +0.23; H, −0.10] indicate that the TS is better described as a proton transfer. Indeed, inspection of the spin densities of 1, the H2-adduct A, and the TS B reveal little spin-depletion at N (−0.12 for 1, −0.13 for A, −0.15 for B) and that the majority of spin density is at uranium (1.19 for 1, 1.18 for A, and 1.24 for B) so N-radical character does not appear to play a significant role in the H2-activation. Following the intrinsic reaction coordinate yields a uranium(V)-imido-hydride complex (C), whose formation is almost athermic (loosely endothermic by 2.0 kcal mol\(^{-1}\)). Complex C can rearrange through a H-atom migration from uranium to parent imido group (transition state D), i.e. undergoing a 1,1-migratory insertion, with a reduction of
uranium oxidation state at this point from V to III. The associated activation barrier is 32.1 kcal mol\(^{-1}\) from C (34.1 from the start point). The height of this barrier is due to the need of the hydride to be transferred as a proton to the nucleophilic imido group. However, this barrier is kinetically accessible and in-line with the slow reaction observed experimentally. This TS yields trivalent 6 that is thermodynamically stable (−21.0 kcal mol\(^{-1}\)). However, in the presence of BMes\(_3\), complex 6 can be easily oxidised into tetravalent 4 in a process that can be considered to be an essentially athermic electron transfer process since the computed energy difference between 4 and 6 is within the error of the calculation.

In the presence of BMes\(_3\), Fig. 10, the computed reaction pathway is quite different. After the formation of a loosely bonded H\(_2\) adduct, the system reaches an H\(_2\) activation TS, that is reminiscent of FLP complex reactivity. Indeed, at TS 2B, the H\(_2\) molecule interacts in a bridging end-on fashion with the nitride (that is the nucleophile of the FLP) and the borane (that is the electrophile). Unlike TS 2B, the H\(_2\) molecule is very little activated at 2A (1.02 vs 0.83 Å, respectively), and neither the N—H bond (1.68 Å) nor the B—H one (1.69 Å) are yet fully formed. The U—N\(_{\text{nitr}}\) bond distance is similar to that found for 2A (1.81 Å). The associated barrier is relatively low (14.6 kcal mol\(^{-1}\) with respect to the start point) and similar to the σ-bond metathesis mechanism. Therefore, the presence of BMes\(_3\) does not impact the protonation of the strongly nucleophilic nitride that is very reactive. Again, there is essentially no spin-depletion at the nitride (−0.12 for 1, −0.13 for 2A, −0.12 for 2B) and the unpaired spin density is clearly localised at uranium (1.19 for 1, 1.20 for 2A, 1.21 for 2B), which argues against nitride radical character in this reactivity. The FLP TS 2B evolves to the formation of a fully dissociative ion pair whose formation is exothermic (−13.9 kcal mol\(^{-1}\) from start point). From the uranium(V)-imido complex 2C, the formation of trivalent 6 then tetravalent 4 was considered. The first, shown by the grey pathway, implies that the hydroborate (HBMes\(_3\))\(^+\) delivers the hydrogen to the imido (2D\(_1\)). However, this route is not favoured because, like the problem in the absence of BMes\(_3\), the hydride has to be transferred as a proton. The computed barrier of 40.4 kcal mol\(^{-1}\) from 2C (26.5 kcal mol\(^{-1}\) from the start point) is in-line with this. The second possibility, shown by the black pathway, involves a second FLP-type activation of H\(_2\) (2D\(_2\)). The associated barrier is 10.5 kcal mol\(^{-1}\) lower than 2D\(_1\), demonstrating the beneficial role of BMes\(_3\). However, the 2D\(_2\)

![Fig. 8 Reaction cycle for the production of ammonia. Treatment of 7 with sodium azide, KC\(_8\), and two equivalents of B15C5 produces the terminal uranium-nitride 1, which in turn reacts with H\(_2\) and BMes\(_3\) to give 4. Treatment of 4 with Me\(_3\)SiCl, followed by work-up and acidification steps, as indicated by the multiple arrows, produces ammonia. B15C5 = benzo-15-crown-5 ether. Mes = 2,4,6-trimethylphenyl.](image)

![Fig. 9 Computed reaction profile for the conversion of 1 to 6 in the absence of BMes\(_3\) and then conversion to 4 with the addition of BMes\(_3\). The isopropyl groups of the silyl substituents, carbon-bound hydrogen atoms, and [K(B15C52)]\(^+\) cation accommodated in the calculations are omitted for clarity. Bold numbers without parentheses refer to \(\Delta H\) values and numbers in parentheses are \(\Delta G\) values, both quoted in kcal mol\(^{-1}\).](image)
The TS, where the N–H distance is far shorter than in 2B (1.44 Å vs. 1.68 Å) inducing a shorter B–H distance (1.54 Å vs. 1.69 Å). The resulting more compact geometry enhances steric repulsion that increases the activation barrier. The 2D₂ TS yields ultimately tetravalent 4 (via trivalent 6) whose formation is exothermic by 21.3 kcal mol⁻¹.

**Discussion**

Despite exhaustive attempts, we find no evidence for any reactivity between the uranium(VI)-nitride 2 and H₂ irrespective of whether borane promoters are present or not. However, this is not surprising since prior computational studies have suggested that the U≡N triple bond is rather covalent, possibly even more so than group 6 congeners, and so it conforms to the general phenomenon that many metal-nitrides, and especially high oxidation state electron-poor ones, are exceedingly unreactive. To date, CO, CO₂, and CS₂ have been found to react with H₂, the mechanisms of which sharply diverge with or without BMes₃, is surprising and notable because the 5f¹ uranium(V) ion in 1 is high oxidation state and cannot be considered to be electron-rich nor low-coordinate. Indeed, the only example of any molecular uranium-nitride reacting with H₂ is the diuranium(IV)-nitride-cesium complex [Cs₂[U(OSi[OBu]₃)₃]₂(μ-N)][7] here, the product is the bridging parent imido-hydride complex [Cs₂[U(OSi[OBu]₃)₃]₂(μ-NH)(μ-H)] and this transformation is enabled by the bridging, polar nature of the nitride and polymeric cooperativity effects. However, that chemistry stops at the imido-hydride stage, or reverts to nitride and H₂, and does not proceed to the H-atom 1,1-migratory insertion stage to give an amide. When terminal M≡N triple bonds have been found to react with H₂ it is with 4d⁴ Ru(IV)₂ or 5d⁴ Os(IV)² to give NH₃ and 5d⁶ Ir(III)² to give Ir–NH₂, since these are the only nitrides that are low-coordinate and sufficiently activated and electron-rich enough to reduce the M≡N triple bond orders by populating anti-bonding interactions. This electron-rich activation is not applicable to 1 being only 5f¹ and that f-electron is in principle nonbonding. However, the nitride is a very strong donor ligand that we have previously shown can modulate the m₃ groundstate of uranium depending how strongly it can donate. Specifically, the nitride forms σ- and π-bonds with the l = 0 and l = 1 5f-orbitals, but also interacts with the l = 2 and l = 3 5f-orbitals where the 5f-electron must reside and thus the supposedly nonbonding 5f¹ electron would seem to be not entirely innocent in this circumstance due to an inevitable anti-bonding interaction. Nevertheless, that a metal-nitride of oxidation state as high as +5 and valence electron number as low as one is capable of activating H₂ without utilising ancillary ligand reactivity and H-atom shutting is unprecedented. Since the reaction profile calculations do not support the notion of nitride radical character promoting the observed and unexpected reactivities, we suggest that this is due to a combination of the 5f-electron in 1 not being wholly nonbonding, and also that the uranium(V)-nitride bond is actually more polar than transition metal analogues.

The reaction profile calculations combined with experimental observations provide an internally consistent account of the reactivity reported here. It is clear from experiment that 1 does not bind BMes₃, unlike BPh₃, presumably on steric grounds presenting the potential for FLP chemistry that is intuitively...
invoked when considering the steric demands of TrenTIPS and BMes3. When 1 is reacted with H2 in the presence of BMes3, the [U(TrenTIPS)(N)]− and BMes3 components constitute the FLP that can form an encounter complex with H2 and the computed intermediate 2A and TS 2B are clear evidence for a FLP encounter complex, which facilitates the splitting of H2, confirming bona fide FLP reactivity and introducing actinide chemistry to the pantheon of FLP reactivity. Although the conversion of 2C and (HBMes3)− to 6 and BMes3 is thermodynamically favourable, it is kinetically the least feasible route to occur due to the inherent barrier of a hydride being a proton source, and instead it appears that a second FLP activation of H2 occurs along with oxidation of 6 to give 4, which is thermodynamically little different to the previous outcome but kinetically more accessible. Within the error of the calculation the oxidation of 6 to 4 is essentially athermic and likely driven by the strongly reducing nature of the uranium(III) ion in 6 coupled to its electron-rich nature. The two-electron reduction on going from 1 to 6 is entirely consistent with the two-electron redox chemistry of H2, and indeed the one-electron oxidation of 6 to 4 is simply a sacrificial one-electron reduction of BMes3 to BMes3−.

The importance of two FLP reaction steps in the conversion of 1 to 6 and then 4 underscores the importance of the facilitating role that FLP chemistry plays in the hydrogenation of 1. However, more remarkable is that fact that the FLP component is actually not mandatory for hydrogenation of the U≡N triple bond to occur, though its absence does slow the reaction significantly demonstrating the facilitating role of the FLP mechanism since the main origin of this impediment is that formally a proton has to evolve from a hydride. In the absence of an FLP mechanism H2 undergoes a direct 1,2-addition across the U≡N triple bond to give a H−U≡N−H unit that is reminiscent of the aforementioned reactivity of [Ca[U(OSi(µ4-Bu)3]2(µ-N)]47 when their terminal vs bridging natures, respectively, are taken into account. The reactivity of 1 is also reminiscent of aspects of recently reported mechanistic studies of the reaction of uranium(III) with water66, and it is germane to note that concerted two-electron redox chemistry at uranium remains a relatively rare phenomena29,36,67 with one-electron processes dominating. The reactivity of 1,2-addition at 1Effective H−H heterolysis to generate H+ and H−, consistent with the polarising nature of the U≡N triple bond. Interestingly, the production of the final U(III)-NH2 linkage in 6 from pentavalent 1 by H-atom 1,1-migratory insertion, consistent with the two-electron reducing nature of H2 since nucleophilic nitrides tend to react without changing metal oxidation state, is reminiscent of the reactivity of uranium(VI)-nitrides under photolytic conditions, where by a Ru2CH/UVIN combination, via a Ru(C)/UV−N→H intermediate converts to U(VI)-N(H)CR3, since both involve two-electron reductions at uranium overall37,42,48. The reactivity of 1 with H2 has parallels to the reactivity of the ruthenium(VI)-nitride complex [Ru(N(CH2CH2PHBu)_2)2(N)] with H2 to give NH2,26, but with some important differences. The Ru-complex initially reacts with H2 across the Ru-Namide not Ru-Nnitride bond, so like many nitrides when reactivity occurs it is with the ancillary ligand not the metal-nitride linkage itself as is the case with 1. However, the Ru-complex does at a later stage transfer a H-atom from Ru to an imido group to form a Ru-NH2 group like C2/C. In contrast, the iridium(III)-nitride complex [Ir(NC5H4H2-2,2′-C(Me)=N=C6H6-Pr5+C6H3)](N) is reported to undergo concerted reactivity with H2 to directly afford an amide and no prior coordination of H2 to the Ir centre28. Looking more widely to sulfido chemistry, the complex [Ti(η5-C6Me6)2(S)(NC5H4)] reacts with H2 to give the hydrosulfide-hydride [Ti(η5-C6Me6)(SH)(H)]58,69, providing a parallel to the 1,2-addition of H2 across the U≡N triple bond of 1, but unlike 1 the titanocene reactivity halts at the hydrosulfide-hydride formulation and does not undergo a subsequent H-atom 1,1-migratory insertion since that would require formation of SH2 and formally the unfavourable reduction of titanium(VI) to titanium(II). So, the reactivity of 1 displays similar and divergent reactivity pathways to known transition metal-nitride reactivity, but combines 1,2-addition and 1,1-migratory insertion steps where transition metals tend to execute either 1,2-additions or 1,1-insertions at the M≡E bond, but are not capable of executing both together.

The reactivity of 4 with BPh3 and H2 is noticeable, though complex because it would seem products react to give reactants, because again it invokes the notion of FLP chemistry whereby weakly coordinated [U(TrenTIPS)]4+ and [H2NBPh3]− components are sufficiently activated to cleave H2 to give H2NBPh3. While this is currently of no practical use it demonstrates the potential for further FLP hydrogenolysis chemistry to convert the parent amide to ammonia. However, we have demonstrated a reaction cycle, where azide is converted to nitride, which undergoes hydrogenolysis to amide, and the amide can be quenched by acid to give ammonia. Thus, overall a nitride has been hydrogenated to ammonia, and the experimentally and computationally supported proposed reactivity mechanisms contribute to our wider understanding of the reactivity of uranium-nitrides toward H2 in heterogeneous Haber Bosch and ATF scenarios.

In summary, while the uranium(VI)-nitride 2 is apparently inert with respect to reacting to H2, the uranium(V)-nitride 1 is not, suggesting that the 5f-electron of the latter is not entirely nonbonding and that the nitride imposes a strong ligand field on uranium. The absence of reactivity for 2 is entirely in-line with the lack of reactivity for high oxidation state metal-nitrides generally, but the latter is not and is notable for being neither low-coordinate nor electron-rich, which are the two requirements previously common to all terminal metal-nitrides that react with H2, yet it is reactive. This study reveals two distinct H2-activation mechanisms. When the borane BMes3 (Mes=2,4,6-trimethylphenyl) is present a FLP mechanism operates where two H2 heterolysis events and a borane reduction step sequentially combine to furnish a U(VI)-NH2 product, and this, to the best of our knowledge, is the first demonstration of the application of bona fide FLP reactivity to actinide chemistry. When the borane is absent, direct 1,2-addition of H2 across the U≡N triple bond to give a H−U≡N−H intermediate followed by H-atom migration produces a U(III)-NH2 product that is easily oxidised to U(V)-NH2. The direct hydrogenolysis addition is slower than the FLP-mediated mechanism, demonstrating the facilitating role of FLPs. We find evidence that treating the U(VI)-NH2 product with BPh3 and H2 produces further FLP hydrogenolysis reactivity, since H2NBPh3 has been detected in reaction mixtures, but this is reversible and produces products that react to give the starting materials. We have demonstrated an azide to nitride to amide to ammonia reaction cycle, supported by overall hydrogenation involving hydrogenolysis and electrophilic quenching steps. Thus, overall a nitride has been converted to ammonia, and the experimentally and computationally supported proposed reactivity mechanisms inform our understanding of the reactivity of uranium-nitrides towards H2 in heterogeneous Haber Bosch and ATF scenarios.

**Methods**

**General.** Experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using Schlenk-line and glove-box techniques. All solvents and reagents were rigorously dried and deoxygenated before use. Compounds were variously characterised by elemental analyses, NMR, FTIR, EPR, and UV/Vis/NIR electronic
absorption spectroscopies, single crystal X-ray diffraction studies, Evans and SQUID magnetometry methods, and DFT computational methods.

**Preparation of [U(TrenTIPS)(NBpH3)][K(B15C5)2] (3)**

Toluene (20 ml) was added to a stirring mixture of 1 (0.54 g, 0.37 mmol) and BpH3 (0.09 g, 0.37 mmol). The resulting mixture was stirred for 16 h to afford a brown precipitate. The mixture was briefly heated to reflux and filtered. Volatiles were removed in vacuo. The resulting brown solid subsequently identified as 3 was washed with pentane (3 × 5 ml) and dried in vacuo. Yield of 3: 0.42 g, 66%. X-ray quality crystals were grown in benzene solution at room temperature. Anal. calcd for C16H28N3. X-ray quality crystals of 3. (0.5 ml) was degassed and exposed to an atmosphere of H2. The brown solution was analysed1H NMR spectroscopy, revealing the presence of NH4Cl. The resulting brown solid subsequently identified as 3 was washed with pentane (3 × 5 ml) and dried in vacuo. Yield of 3: 0.39%. 1H NMR (C6D6, 298 K): δ 3.915 (s, 6 H, CH3), 10.69 (s, 6 H, Ar-H). 7.26–7.96 (br m, 14 H, Ar-H), 4.47–4.20 (m, 32 H, OCH3), 7.02 (s, 5 H, 5H-Pri-C), 4.59 (s H, CH2CH3), 1.62 (s, 3 H, CH3). δ 7.30 ppm. Ammonia formation after addition of 1 equivalent of HCl to [U(TrenTIPS)(NH2BPh3)] (8)

Ammonia formation after addition of 1 equivalent of HCl to [U(TrenTIPS)(NH2BPh3)] (8) (NHD) (4). Complex 4 (0.05 g, 0.04 mmol), formed from the reaction of 1 with D2 in the presence of BMes3, was treated with 1.2 ml of a 0.05 M HCl solution in THF/EtO (0.06 mmol) and stirred for 2 h at room temperature. All volatiles were then vacuum transferred onto a 2 M HCl solution in Et2O (2 ml). Volatiles were removed in vacuo and the resulting white solid was dissolved in 0.6 ml of d6-DMSO to quantify the amount of ammonia present using 1H NMR spectroscopy (quantification using sealed capillary insert of 2.5-dimethylfuran in d6-DMSO). Integration of the NH4+ multiplet (7.30 ppm) revealed 46% NH4HCl. The 1H NMR spectrum revealed the presence of a broad resonance at 7.12 ppm. Addition of 10 µl of H2O gave complete proton/deuterium exchange, as the resonance at 7.12 ppm in the 1H NMR spectrum disappeared and a NH4+ 1:1 triplet (7.28 ppm, JNH3 = 51 Hz) was formed, integration of the triplet revealed 52% NH4Cl.

Ammonia formation after addition of 1 equivalent of HCl to [U(TrenTIPS)(NH2BPh3)] (8) (NHD) (5) [K(B15C5)2] (6). Complex 6 (0.03 g, 0.021 mmol) was treated with 2.1 ml of a 0.01 M HCl solution in THF/EtO (0.02 mmol) and stirred for 2 h at room temperature. All volatiles were then vacuum transferred into a 2 M HCl solution in Et2O (2 ml). Volatiles were removed in vacuo and the resulting white solid was dissolved in 0.6 ml of d6-DMSO to quantify the amount of ammonia present using 1H NMR spectroscopy (quantification using sealed capillary insert of 2.5-dimethylfuran in d6-DMSO).39 Analysis of the brown solid residue after distillation of the volatiles revealed the presence of 7 in 1–5% yield with TrenTIPPH3 as the main product. Integration of the NH4+ multiplet (7.30 ppm) revealed 35% NH4HCl. The 1H NMR spectrum revealed the presence of a broad resonance at 7.12 ppm. Addition of 10 µl of H2O gave complete proton/deuterium exchange, as the resonance at 7.12 ppm in the 1H NMR spectrum disappeared and a NH4+ 1:1:1 triplet (7.28 ppm, JNH3 = 51 Hz) was formed, integration of the triplet revealed 46% NH4Cl.

**Synthesis of [U(TrenTIPS)(NBpH3)] (3)** (Toluene). Toluene (20 ml) was added to a stirring mixture of 1 (0.60 g, 0.23 mmol) and BpH3 (0.06 g, 0.23 mmol). The resulting mixture was heated to re dissolve the mixture. The filtered mixture was washed with pentane (2 × 5 ml) and dried in vacuo. Yield of 3: 0.42 g, 66%. 1H NMR (C6D6, 298 K): δ 3.915 (s, 6 H, CH3), 10.69 (s, 6 H, Ar-H). 7.26–7.96 (br m, 14 H, Ar-H), 4.47–4.20 (m, 32 H, OCH3), 7.02 (s, 5 H, 5H-Pri-C), 4.59 (s H, CH2CH3), 1.62 (s, 3 H, CH3). δ 7.30 ppm. Ammonia formation after addition of 1 equivalent of HCl to [U(TrenTIPS)(NH2BPh3)] (8) (NHD) (4). Complex 4 (0.05 g, 0.04 mmol), formed from the reaction of 1 with D2 in the presence of BMes3, was treated with 1.2 ml of a 0.05 M HCl solution in THF/EtO (0.06 mmol) and stirred for 2 h at room temperature. All volatiles were then vacuum transferred onto a 2 M HCl solution in Et2O (2 ml). Volatiles were removed in vacuo and the resulting white solid was dissolved in 0.6 ml of d6-DMSO to quantify the amount of ammonia present using 1H NMR spectroscopy (quantification using sealed capillary insert of 2.5-dimethylfuran in d6-DMSO). Integration of the NH4+ multiplet (7.30 ppm) revealed 40% NH4HCl. The 1H NMR spectrum revealed the presence of a broad resonance at 7.12 ppm. Addition of 10 µl of H2O gave complete proton/deuterium exchange, as the resonance at 7.12 ppm in the 1H NMR spectrum disappeared and a NH4+ 1:1 triplet (7.28 ppm, JNH3 = 51 Hz) was formed, integration of the triplet revealed 52% NH4Cl.

Ammonia formation after addition of 1 equivalent of HCl to [U(TrenTIPS)(NH2BPh3)] (8) (NHD) (5) [K(B15C5)2] (6). Complex 6 (0.03 g, 0.021 mmol) was treated with 2.1 ml of a 0.01 M HCl solution in THF/EtO (0.02 mmol) and stirred for 2 h at room temperature. All volatiles were then vacuum transferred into a 2 M HCl solution in Et2O (2 ml). Volatiles were removed in vacuo and the resulting white solid was dissolved in 0.6 ml of d6-DMSO to quantify the amount of ammonia present using 1H NMR spectroscopy (quantification using sealed capillary insert of 2.5-dimethylfuran in d6-DMSO). Integration of the NH4+ multiplet (7.30 ppm) revealed 35% NH4HCl. The 1H NMR spectrum revealed the presence of a broad resonance at 7.12 ppm. Addition of 10 µl of H2O gave complete proton/deuterium exchange, as the resonance at 7.12 ppm in the 1H NMR spectrum disappeared and a NH4+ 1:1:1 triplet (7.28 ppm, JNH3 = 51 Hz) was formed, integration of the triplet revealed 46% NH4Cl.

Ammonia formation after addition of 1 equivalent of DCl to [U(TrenTIPS)(NH2BPh3)] (8) (NHD) (4) (NDCI) (7). Complex 7 (0.04 g, 0.03 mmol) was treated with 2.8 ml of a 0.01 M DCl solution in THF/EtO (0.03 mmol) and stirred for 2 h at room temperature. All volatiles were then vacuum transferred into a 2 M HCl solution in Et2O (2 ml). Volatiles were removed in vacuo and the resulting white solid was dissolved in 0.6 ml of d6-DMSO to quantify the amount of ammonia present using 1H NMR spectroscopy (quantification using sealed capillary insert of 2.5-dimethylfuran in d6-DMSO). Analysis of the brown solid residue after distillation of the volatiles revealed the presence of 7 in 1–5% yield with TrenTIPPH3 as the main product. Integration of the NH4+ multiplet (7.30 ppm) revealed 35% NH4HCl. The 1H NMR spectrum revealed the presence of a broad resonance at 7.12 ppm. Addition of 10 µl of H2O gave complete proton/deuterium exchange, as the resonance at 7.12 ppm in the 1H NMR spectrum disappeared and a NH4+ 1:1:1 triplet (7.28 ppm, JNH3 = 51 Hz) was formed, integration of the triplet revealed 46% NH4Cl.
5 ml and dried in vacuo. Yield of 8: 0.16 g, 62%. Anal. calc. for C$_3$H$_7$N$_5$Si$_3$: C, 55.26; H, 8.37; N, 6.32%. Found: C, 55.52; H, 8.16; N, 5.91%. NMR spectroscopy reveals that when isolated 8 is dissolved in solution it dissociates to 4 and free BPH$_3$, and also trace H$_2$NBPH$_3$ and 9, but this equilibrium can be manipulated by cooling samples favoring the formation of 8 so a variable-temperature NMR study was performed, see below. The presence of H$_2$NBPH$_3$ could not be unequivocally confirmed in the $^{1}H$ NMR spectrum due to its low concentration level in a spectrum dominated by para-magnetic species, but its presence is confirmed by $^{11}$B NMR spectroscopy. Trace resonances corresponding to reported data for 9 could be observed\cite{20}, $^{11}$B/$^1$H NMR (CD$_2$D$_2$, 298 K): $^{11}$B 67.5 (BPH$_3$), $-3.2$ (H$_2$NBPH$_3$), $-55.2$ (U-H$_2$NBPH$_3$). FTIR: $\nu$/cm$^{-1}$: 3292 (w), 3228 (w), 3044 (w), 2938 (m), 2886 (m), 2861 (m), 1590 (w), 1502 (w), 1461 (m), 1428 (m), 1372 (m), 1339 (w), 1316 (w), 1270 (m), 1238 (m), 1166 (w), 1133 (w), 1116 (w), 1047 (m), 1010 (m), 988 (m), 925 (s), 880 (w), 816 (w), 731 (s), 701 (s), 670 (s), 632 (s), 596 (m), 565 (m), 554 (m), 514 (s) (Evans method, CD$_2$D$_2$, 298 K): 2.96 $\mu$m.

Variable-Temperature NMR Study of 8. A brown solution of 4 (0.04 g, 0.05 mmol) in $d_6$-toluene (0.3 ml) was added to BPH$_3$ (0.01 g, 0.05 mmol) in $d_6$-toluene (0.2 ml). The brownish black solution was analysed by $^1$H and $^{11}$B{$_1^1$H} NMR method for N-15 labeling. Chem. Commun. 9, 126–127 (2003).

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