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Catalytic Recycling of a Th-H Bond *via* Singly or Doubly Hydroboration of Inactivated Imines or Nitriles

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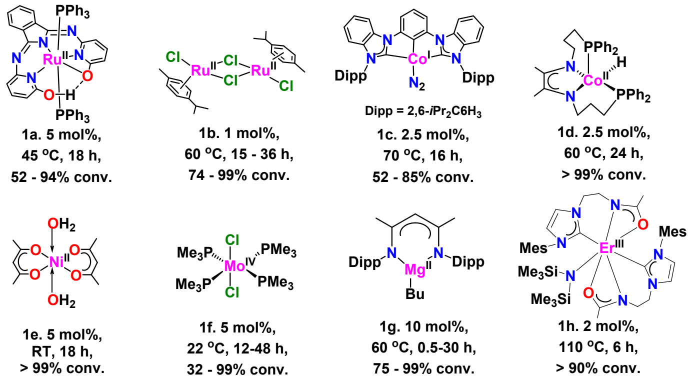
ABSTRACT: The catalytic activity of the metallacycle thorium amide $[(Me_3Si)_2N]_2Th[\kappa^2\text{–}(N,C)\text{–}CH_2Si(CH_3)_2N(SiMe_3)]$ (**Th1**) is presented for the selective dihydroboration of nitriles (–C≡N) with pinacolborane (HBpin). Using significantly low catalyst loading (0.1 mol%), the dihydroborated amines were achieved by the hydroboration of the –C≡N triple bond attached with aromatic, aliphatic and heteroatom backbones with high turnover frequency (TOF) as compared to all the reported homogeneous metal catalysts in this reaction. In addition, for aldimines (–C=N–), the hydroboration precatalyst **Th2** has been synthesized by the protonolysis of a seven-membered N-heterocyclic iminato ligand (LH) and **Th1**. **Th2** crystal structure and its performance in the synthesis of hydroborated secondary amine is also here presented. Detailed kinetic studies, thermodynamic and stoichiometric experiments provided us with cumulative evidence supporting the proposed mechanism for the aforementioned reactions.

KEYWORDS. Organoactinide catalyst, Thorium, Nitrile, Imine, Hydroboration.

Introduction

Primary and secondary amines and their derivatives are extensively present in natural products, drugs, agrochemicals, polymers, dyes, textiles and in many more industrial and academic encounters.[1] Direct base–promoted N–alkylation of amines with alkyl halides or alcohols,[2] alkylative aminations,[3] reductive aminations of carbonyl compounds,[4] hydroamination of unsaturated hydrocarbons with amines,[5] are the most conventional techniques to synthesize amines. Still, expensive starting materials, generation of huge organic wastes, and exhaustive alkylation impede, in many cases, the utility of the above procedures.[6] Hence, in the last few decades, metals or metal-non–metal moieties catalyzed hydrogenation of nitriles using molecular hydrogen (H_2) has become a very advantageous method to produce primary amines.[7] However, the low selectivity,[8] necessity of high H_2 pressure,[9] copious reagents,[10] formations of inorganic by–products[10] again cripple the wide usefulness of these methods. Alternatively, the catalytic hydroelementation process such as hydroboration or hydrosilylation came to limelight for mild and selective reduction of nitriles to provide primary amines.[11] Although the catalytic hydrosilylation commonly affords a mixture of monosilylated imine and disilylamine products, the catalytic hydroboration produces diboronated amines as the sole product, that are easily converted into the corresponding primary amines.[12] Lately, the catalytic hydroboration of nitriles has started to be explored as a strategic method for the synthesis of amines.[13] The complexes that are known, until now, able to perform the double hydroboration of nitriles are summarized in Scheme 1. Szymczak[13a] and Gunanathan[13b] reported a proton–switchable bifunctional Ru(II) complex and $[Ru^{II}(p\text{–cymene})Cl_2]_2$, respectively, to catalyze nitrile hydroboration (Scheme 1a and 1b). Fout[13c] and Trovitch[13d] reported Co(I) and Co(II) complexes that catalyzed nitrile hydroboration, respectively (Scheme 1c and 1d). Shimada and co-workers demonstrated that bis(acetylacetonato)nickel(II) afforded the synthesis of diboronated amines (Scheme 1e).[13e] Hill and co-workers disclosed an Mg(II)–catalyzed hydroboration of nitriles (Scheme 1g).[13f] The interesting Mo(IV) complex that catalyzed the nitrile hydroboration was disclosed by Nikonov's group (Scheme 1f),[13g] and the lanthanide N–heterocyclic carbene–Er(III) complex was reported by Wang for the hydroboration of nitrile substrates (Scheme 1h).[13h]

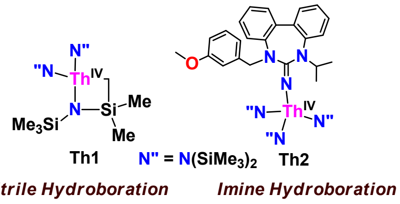


Scheme 1 Precatalysts reported in the literature for nitrile hydroboration.

The synthesis of secondary amines that can be obtained from the catalytic hydrogenation of double bonds of imines, −C=N−, turned out to be an effective method in recent days.[14] The reduction of imines can be achieved using metal hydride reagents, such as BH_3, $LiAlH_4$ or $NaBH_4$, but these reagents remain somewhat unappealing due to poor reaction yields and selectivity.[15] Instead, alkaline earth metals and transition metals (Ca, Ru, Rh, Ir, Pd, Pt, Au) that catalyzed the hydrogenation of imines has been extensively explored.[16] Like in the case of nitriles, the hydroboration of imines is also earning eminence over the traditional methods of direct hydrogenation due to the mild reaction conditions and the higher selectivity in the synthesis of chiral amines. In 1995, bidentate phosphine–gold(I) complexes with catecholborane catalyzed the hydroboration of imines and it was the first disclosure by Baker et al.[17] Afterward, few reports have been published on the hydroboration of imines catalyzed by alkaline earth metals, transition metals, and some Lewis bases.[18,13b]

Despite having strong potentials, organoactinide compounds have not been greatly exploited in the field of catalysis[19] in comparison to stoichiometric reactions[20]. Recently, we have developed some thorium precatalysts for the regioselective and chemoselective hydroboration of pyridines, heterocyclic systems, aldehydes/ketones, and carbodiimides.[21]

In this work we disclosure the unexpected extraordinary catalytic activity of the metallacycle thorium amide complex $[(Me_3Si)_2N]_2Th[\kappa^2–(N,C)–CH_2Si(CH_3)_2N(SiMe_3)]$ (**Th1**) (Scheme 2) in the hydroboration of nitriles using pinacolborane (HBpin) for the synthesis primary amines with the highest turnover frequency (TOF), among the homogeneous catalysts, reported in the literature. Likewise, the embedment reaction of an N–heterocyclic iminato ligand (LH) with complex **Th1** affords the synthesis of the corresponding actinide complex **Th2** (Scheme 2), which was found to be an outstanding precatalyst for the hydroboration of imines. In addition to the scope of the reactions, detailed stoichiometric and kinetic studies have been performed to investigate the reaction mechanism for both nitriles and imines hydroborations.



Scheme 2 Thorium precatalysts used in this work.

Table 1 Reaction optimization.[a]

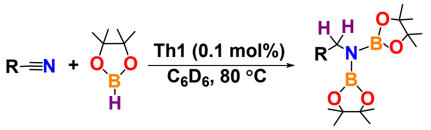
Entry	Substrate	Boranes (equiv.)	Cat. (mol%)	Time (h)	Temp. (°C)	Yield[b] %
1	PhCN	HBpin (2.2)	**Th1** (1)	4	25	100
2	PhCN	HBpin (2.2)	–	24	25	–
3	PhCN	HBpin (2.2)	**Th1** (1)	0.25	80	100
4	PhCN	HBpin (2.2)	**Th1** (0.1)	3	80	95
5	PhCN	HBpin (2.2)	**Th1** (0.1)	4	80	100
6	PhCN	HBcat (2.2)	**Th1** (0.1)	16	80	100
7	PhCN	HBcat (2.2)	–	24	80	–
8	PhCN	9-BBN (2.2)	**Th1** (0.1)	24	80	15
9	PhCN	9-BBN (2.2)	–	24	80	5
10	PhCH=NPh	HBpin (1.1)	**Th1** (1)	24	25	–
11	PhCH=NPh	HBpin (1.1)	**Th1** (1)	36	80	52
12	PhCN	HBpin (2.2)	Th2 (1)	3	80	90
13	PhCH=NPh	HBpin (1.1)	**Th2** (1)	24	80	95
14	PhCH=NPh	HBpin (1.1)	**Th2** (1)	24	25	–
15	PhCH=NPh	HBpin (2.2)	**Th2** (1)	8	80	100

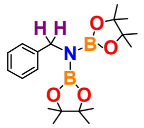
[a]Reaction condition: **Th1**/**Th2**, PhCN/PhCH=NPh, and boranes in C_6D_6 inside a J–Young teflon valve-sealed NMR tubes at variable temperature; [b]By ^{1}H NMR analysis.

Results and Discussions

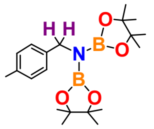
Catalytic Hydroboration of Nitriles. To evaluate the catalytic efficiency of the **Th1** complex for the hydroboration of nitriles, initial exploratory experiments were carried out using benzonitrile (1 mmol), pinacolborane (HBpin, 2.2 mmol) and the precatalyst **Th1** (0.01 mmol) inside a J-Young Teflon valve-sealed NMR tube at room temperature in C_6D_6. Full conversion (100%) to the corresponding dihydroborated amine product **2a** was observed after 4 h (entry 1, Table 1). It is important to indicate that no hydroborated product was observed in the absence of the actinide complex **Th1** (entry 2, Table 1). Raising the reaction temperature to 80 °C expedited the rate of reaction and 100% conversion was detected within 15 min (entry 3, Table 1). The reduction of the catalyst loading of the model reaction from 1 to 0.1 mol% provided 100% and 95% conversion after 4 h (TOF: 250 h^{-1}) and 3 h (TOF: 317 h^{-1}), respectively at 80 °C (entries 4 and 5, Table 1). The activity of the thorium complex **Th1** for the nitrile hydroboration was also examined in the presence of other hydroboranes, such as catecholborane (HBcat) and 9-borabicyclo(3.3.1)nonane (9-BBN). The reaction of benzonitrile (1 equiv) and HBcat (2.2 equiv) in the presence of 0.1 mol% **Th1** afforded 100% conversion after 16 h (entry 6, Table 1) and no hydroborated product was obtained in the

Table 2 **Th1** catalyzed hydroboration of nitriles with HBpin.^{a}

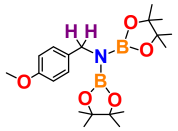




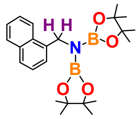
2a (3 h, 95%)
TOF: 317 h^{-1}



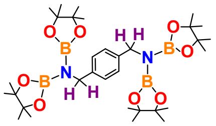
2b (3 h, 98%)
TOF: 327 h^{-1}



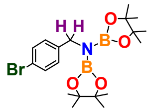
2c (2.5 h, 100%)
TOF: 400 h^{-1}



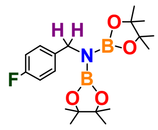
2d^b (6 h, 75%)
TOF: 25 h^{-1}



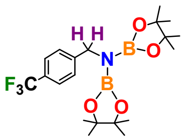
2e^c (6 h, 88%)
TOF: 147 h^{-1}



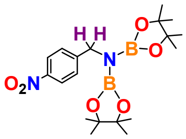
2f (3 h, 93%)
TOF: 310 h^{-1}



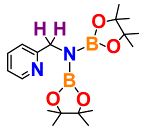
2g (5 h, 94%)
TOF: 192 h^{-1}



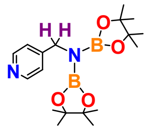
2h (6 h, 90%)
TOF: 150 h^{-1}



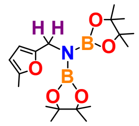
2i^b (10 h, 100%)
TOF: 20 h^{-1}



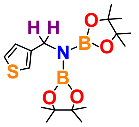
2j (24 h, n. r.)



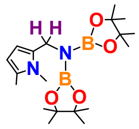
2k (4 h, 100%)
TOF: 250 h^{-1}



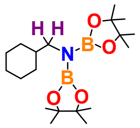
2l (6 h, 75%)
TOF: 125 h^{-1}



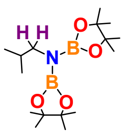
2m (6 h, 75%)
TOF: 125 h^{-1}



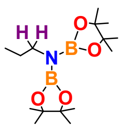
2n (4 h, 98%)
TOF: 245 h^{-1}



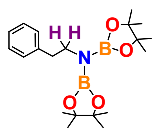
2o (2 h, 100%)
TOF: 500 h^{-1}



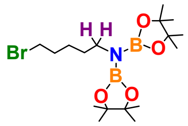
2p (2 h, 100%)
TOF: 500 h^{-1}



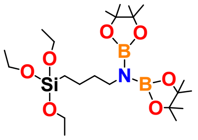
2q (2 h, 100%)
TOF: 500 h^{-1}



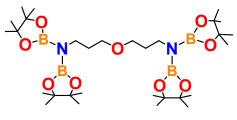
2r^b (8 h, 80%)
TOF: 20 h^{-1}



2s (8 h, 92%)
TOF: 115 h^{-1}



2t (8 h, 95%)
TOF: 120 h^{-1}



2u^c (8 h, 90%)
TOF: 112 h^{-1}

^{a}Reaction condition: nitriles (1 mmol), HBpin (2.2 mmol), and precatalyst **Th1** (0.001 mmol) at 80 °C in C_6D_6 (0.6 mL); yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. ^{b}0.005 mmol **Th1** were used. ^{c}0.002 mmol **Th1** and 4.4 mmol HBpin were used.

absence of the actinide catalyst (entry 7, Table 1). In comparison, the reaction of benzonitrile (1 equiv) and 9-BBN (2.2 equiv.) 15% and 5% of the double hydroborated products was obtained after 24 h in presence of 0.1 mol% **Th1** or with no catalyst, respectively (entries 8 and 9, Table 1), indicating that 9-BBN can perform the reaction, however in a sluggish mode, unless larger amount of the precatalyst is used.

Hence, we continue to explore the substrate scope for the actinide complex **Th1** under the optimized reaction conditions (Table 2). The quantitative yields of the dihydroborated amines obtained from the corresponding nitriles were obtained by following the reaction via ^{1}H NMR analysis (see supplementary material). However, quantitative amounts of the double hydroborated amines can be obtained, in a similar fashion, using benzonitrile (0.1 mol), HBpin (0.22 mol), and **Th1** (1×10^{-4} mmol) at 80 °C in C_6H_6 (60 mL) in a Schlenk's vessel after 3 h. As presented in Table 2, electron-rich aromatic nitriles bearing electron-donating groups such as *p*-Me (entry 2b) and *p*-OMe gave 98% (entry 2c) and 100% conversion after 3 h (TOF: 327 h^{-1}) and 2.5 h (TOF: 400 h^{-1}), respectively. The rate of hydroboration of the −C≡N bond decorated with polycyclic aromatic rings, such as 1-naphthonitrile (entry 2d) is sluggish in comparison to benzonitrile. Under the optimized conditions, the reaction stopped after 65% conversion, whereas with 0.5 mol% catalyst loading, 75% (TOF: 25 h^{-1}) conversion was obtained after 6 h. Electron-deficient aryl nitriles are generally less reactive with HBpin than the corresponding electron rich counterparts. Hence, under the optimized reaction conditions, 1,4-dicyanobenzene (entry 2e) afforded 88% after 6 h (TOF: 147 h^{-1}). Similarly, the reactions of HBpin with 4-fluorobenzonitrile (entry 2g) progressed less efficiently in comparison to 4-bromobenzonitrile (entry 2f) affording the corresponding dihydroborated product with 94% yield after 5 h (TOF: 192 h^{-1}) and 3 h (TOF: 310 h^{-1}), respectively. In the reaction of 4-(trifluoromethyl)benzonitrile (entry 2h) and HBpin, 90% yield is obtained after 7 h (TOF: 150 h^{-1}). The incorporation of a nitro group ($-NO_2$) in the aromatic ring further diminished the rate of the reaction by manifolds. Since the hydroboration reaction of 4-nitrobenzonitrile (entry 2i) was too slow with 0.1 mol% catalyst loading, the reaction was performed with 0.5 mol% of the thorium complex **Th1**, and 100% conversion was afforded after 10 h (TOF: 20 h^{-1}). The reaction proceeded selectively, at the nitrile position, leaving the nitro group unreacted (Figure S31). Intriguingly, no product was observed for picolinonitrile (entry 2j); the lack of reactivity for the pyridine analog it might be attributed to a catalyst deactivation via metal coordination to the pyridine nitrogen,[22] however similar systems with furan and thiophene moieties, did not show such behavior (*vide infra*). Performing the reaction with 4-pyridinecarbonitrile, 100% conversion was obtained after 4 h (TOF: 250 h^{-1}) (entry 2k) (Figure S33). Moreover, the hydroboration of the −C≡N group attached to other heteroaromatic rings, such as, 5-methyl-2-furonitrile (entry 2l), 3-thiophenecarbonitrile (entry 2m) and 1,5-dimethyl-2-pyrrolecarbonitrile (entry 2n) proceeded efficiently to give the corresponding dihydroborated amines in 75% (6 h, TOF: 125 h^{-1}), 75% (6 h, TOF: 125 h^{-1}) and 98% (4 h, TOF: 245 h^{-1}) overall yields, respectively. The scope of the substrates was expanded by performing the reaction with more challenging inactive aliphatic nitriles. As shown in the literature, the known catalysts are less reactive for aliphatic substrates.[23] However, in our case, the thorium precatalyst, **Th1**, showed remarkable turnover frequencies for the corresponding aliphatic substrates, comparable to those obtained for the aromatic nitriles. The reactions of HBpin with cyclohexanecarbonitrile (entry 2o), isobutyronitrile (entry 2p) and propionitrile (entry 2q) provided 100% conversion within 2 h (TOF: 500 h^{-1}). Other types of aliphatic nitriles including benzyl cyanide (entry 2r), bromopentanenitrile (entry 2s), 3-cyanopropyltriethoxysilane (entry 2t), 5- and 2-cyanoethyl ether (entry 2u) afforded the dihydroborated products in good yields, 80% (TOF: 20 h^{-1}), 90% (TOF: 115 h^{-1}), 95% (TOF: 120 h^{-1}) and 90% (TOF: 112 h^{-1}), respectively. To the best of our knowledge, our precatalyst **Th1** exhibited the highest catalytic activity as compared with any other homogeneous catalysts reported in the literature for the nitrile dihydroboration reaction.

Catalytic Hydroboration of Imines. We commenced the imine hydroboration studies by examining the catalytic activity of **Th1**. with N,1-diphenylmethanimine, PhCH=NPh. Initial evaluation revealed that **Th1** (1 mol%) afforded only 52% of the reduced product **3a** at 80 °C after 36 h (entries 10 and 11, Table 1). After some catalytic screening, we subsequently changed the course study to study the performance of the new complex **Th2** (Scheme 2) in the imine hydroboration. **Th2** was prepared by the rapid protonolysis reaction of **Th1** with the neutral seven-membered N-heterocyclic iminato ligand LH (Scheme S2) following to our recent disclosed protocol.[24] The solid-state structure of the precatalyst **Th2** was confirmed by single-crystal X-ray diffraction (Figure 1). The X-ray structural analysis revealed that the central Th(IV) is in a distorted tetrahedral geometry consisting of one seven-membered N-heterocyclic iminato ligand (L) and three N-silylated amido [$-N\{Si(CH_3)_3\}_2$] groups. The ligand (L) binds with the metal in a monodentate fashion, and the remaining three positions are occupied by amido ligands, completing the tetrahedral environment. The N3−C1$_{ipso}$ bond distance is 1.266(5) Å for **Th2**, is analogous to the corresponding bond lengths in related imidazolin-2-iminato complexes indicating that no mesomeric structures donating electron density to the metal is operative from that double bond.[20b] However, the Th−N3 bond distance in complex **Th2** of 2.216(3) Å indicates that the seven-membered N-heterocyclic iminato ligand (L) is attached to the metal as a metalla-cumulene. This mode of bonding is supported by the small bent Th1−N3−C1 angle 164.0(3)° allowing a substantial π donation from the ligand to the metal, generating a double bond between the metal and the imine nitrogen. The X-ray structural analysis revealed alike structures like those reported for other actinide imidazoline iminato complexes.[21b,24b,24e,25]

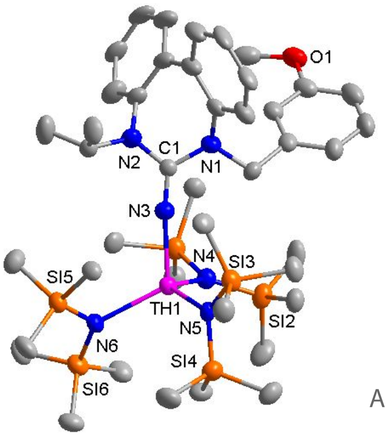


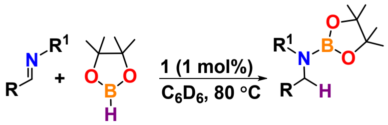
Figure 1 Molecular structure of complex

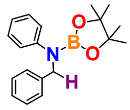
In **Th2** the Th−N$_{imido}$ bond [Th1–N3 2.216(3)] is significantly shorter than the Th−N$_{amido}$ bonds [Th1–N4 2.333(3), Th1–N5 2.351(3), Th1–N6 2.375(3)] and this also supports the observations reported literature[26]. In the presence of 1 mol% of **Th2**, the hydroboration of benzonitrile afforded 90% conversion after 3 h at 80 °C (entry 12, Table 1). Although in nitrile hydroboration the efficacy of **Th2** is not as good as **Th1**, in the imine hydroboration **Th2** showed much higher efficiency as compared to **Th1**. So, we continued our studies with the complex **Th2** for the hydroboration of imines. In the presence of 1 mol% of **Th2**, 95% of the hydroborated product, **3a** was afforded at 80 °C after 24 h (entry 13, Table 1). Attempts to carry out the aforementioned reaction at room temperature (25 °C) shows no reduced product (entry 14, Table 1). However, a twofold increase in the amount of HBpin showed a significant influence in the rate of the reaction; 100% conversion was obtained within 8 h at 80 °C (entry 15, Table 1).

Substituted aldimines (**3b**-**3l**, Table 3) were subjected to the hydroboration reaction in the presence of 1.1 equivalent of HBpin at 80 °C to study the substrate scope capabilities. The quantitative yields of the corresponding hydroborated amines were obtained by following the reaction using ^{1}H NMR spectroscopy. Both aromatic and aliphatic imines afforded the hydroborated secondary amines in good yields (90-100%) in a maximum of 24 h. Overall, the imines comprising electron-donating functionalities increased the rate of the reaction in comparison to the imines decorated with electron-withdrawing groups. Hydroboration of imine [tert-butyl (phenylmethylene)carbamate] with BOC as a protecting group afforded secondary amine product **3m** with 80% conversion after 24 h. The catalytic performance of the **Th2** complex is comparable with other homogeneous metal catalysts reported in the literature for aldimine hydroboration.[18] Interestingly, the precatalyst **Th2** showed no catalytic activity in the hydroboration of ketimines, presumably due to the steric hindrance around the metal complex after complexation.

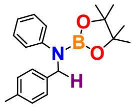
Mechanistic Studies for Nitrile Hydroboration. To gain a more detailed insight into the nitrile hydroboration catalytic cycle and into the activation of the complex **Th1**, stoichiometric, kinetic and temperature dependence studies were performed. The stoichiometric reaction between **Th1** and one equiv of HBpin caused the immediate opening of the 4-membered cyclic structure of **Th1** with the disappearance of its characteristic peaks in the ^{1}H NMR spectrum and afforded the complex spectrum (Figure S70). In addition, no hexamethyldisilazane or pinacolborahexamethyldisilazane were detected in the GC-MS or MALDI spectroscopy, indicating that the pinacolborane has been added to the complex. The simultaneous appearance of a broad peak at δ 5.56 ppm was assigned as the corresponding hydride (Th-H) peak in intermediate [A] (*vide infra*). As expected, the signal at δ 5.56 ppm, is not observed for the reaction of **Th1** with

Table 3 **Th2** catalyzed hydroboration of imines with HBpin.[a]

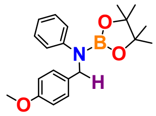




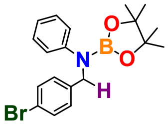
3a (24 h, 95%)



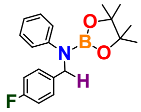
3b (24 h, 97%)



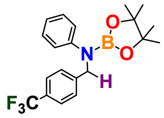
3c (12 h, 100%)



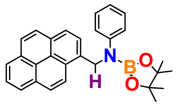
3d (12 h, 100%)



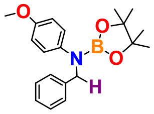
3e (18 h, 100%)



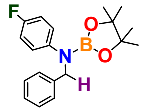
3f (24 h, 82%)



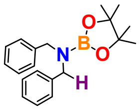
3g (24 h, 90%)



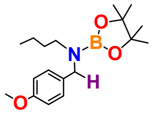
3h (18 h, 98%)



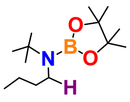
3i (24 h, 85%)



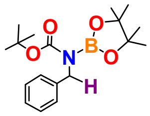
3j (24 h, 92%)



3k (12 h, 100%)



3l (12 h, 100%)



3m (24 h, 80%)

[a]Reaction condition: imines (1 mmol), HBpin (1.1 mmol), and precatalyst **Th2** (0.01 mmol) at 80 °C in C_6D_6 (0.6 mL); yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

DBPin in the ^{1}H NMR (Figure S71). Furthermore, the addition of two equiv. of DBpin in the mixture of {**Th1** + HBpin (1 equiv.)} prompts the gradually disappearance of the signal at δ 5.56 ppm in 24 h (Figure S74). As can be observed, the Th−H signal is slowly exchanging with deuterium affording the corresponding Th−D intermediate. Clearly, this is not a free Th-H moiety, since these hydrides appear downfield (between 16-19 ppm);[27] but indicates a bridged hydride between the B and the Th metal center.[13f] The IR signal at 960 cm^{-1} observed in the reaction mixture of {**Th1** + HBpin (1 equiv.)} was assigned as the bridged Th-H-B moiety (Figure S77).[27] The addition of 2 equiv. of DBpin to the reaction mixture of [{**Th1** + HBpin (1 equiv.)} decreases the intensity of the 960 cm^{-1} signal and gives rise to a new signal at 687 cm^{-1} allotted as Th-D-B moiety (Figure S78).[27] It is important to point out that further addition of HBpin (up to 5 equiv.), to the reaction mixture, does not cause any additional changes as it is observed in the ^{1}H NMR spectra (Figures S72). The addition of one equivalent of PhCN to a mixture of [**Th1** (1 equiv) + HBpin (3 equiv)] immediately gives the dihydroborated product **1a**. In the ^{1}H NMR, there is no signal for the formation of the intermediate imine (PhCH=NBpin) (Figure S75). To be able to distinguish between a mechanism in which the hydroborated imine is eliminated and rapidly added to a Th-H moiety as compared to a mechanism in which the hydroborated imine moiety never leaves the complex coordination sphere, the reaction of **Th1**, (1 equiv) + HBpin (1 equiv) and PhCN (1 equiv) was performed, yielding a mixture of the hydroborated imine and the double hydroborated amine (Figures S76). This important result indicates that the hydroborated imine is indeed eliminated and is hydroborated more rapidly than the corresponding nitrile.

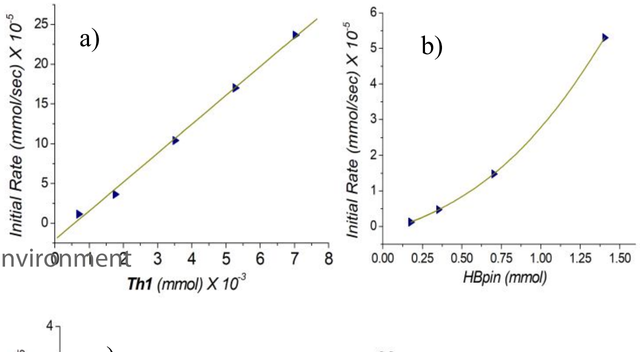
Kinetic measurements indicate that the empirical rate law, observed for the hydroboration of $PhCH_2CN$ catalyzed by complex **Th1** exhibits a first-order dependence on the catalyst, a second-order dependence on HBpin and no dependence on nitrile concentration (Eq. 1) (Figures 2a-c). For the full kinetic equation treatment, please see the Supplementary Information (SI).

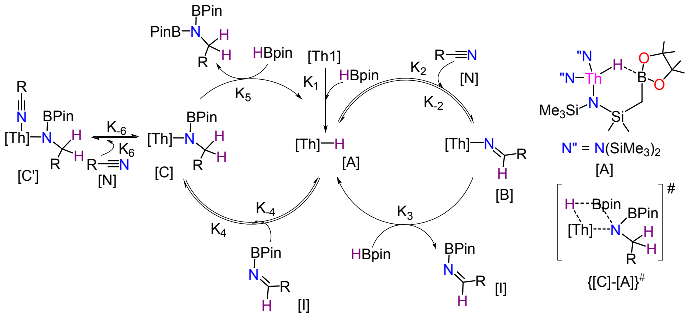
$$\delta p/\delta t = k_{obs} \times [\mathbf{Th1}]^1 [\mathrm{HBpin}]^2 [\mathrm{PhCH_2CN}]^0 \qquad (1)$$

Moreover, activation parameters for the hydroboration of $PhCH_2CN$ by complex **Th1** were determined from the Eyring and Arrhenius plots with $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and E_a values of −47.25 (1.23) e.u., 6.99 (0.44) kcal/mol and 7.66 (0.44) kcal/mol, respectively (Figures 2d, S92–94). The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ data are consistent with a concurrent bond-cleavage and bond-formation events and a very organized four-membered ring rate-determining step, respectively.

Deuterium isotope studies show that the reaction exhibits a KIE (k_H/k_D) of 5.4 (0.08) (Figure S91), indicating that the Th-N(Bpin)(CH_2R)/H-Bpin σ-bond metathesis is the operative turnover-limiting step.

Based on these studies, a plausible hydroboration mechanism for nitriles is proposed which consists of two catalytic cycles (Scheme 3). The activation of the reaction cycles is first achieved by the quick insertion of the HBpin into the thorium metallacycle **Th1** giving rise to the active thorium hydride complex [A]. Cycle 1 starts with the extremely fast insertion of the Th-H motif of complex [A] into the –C≡N moiety allowing the formation of the intermediate complex [B]. However, as shown in the stoichiometric reactions, in the presence of HBpin, the subsequent Th-N=C(H)R/H-B σ-bond metathesis regenerates the active complex [A] with the concomitant formation of the intermediate imine (PhCH=NBpin). Simultaneously, the activation of the second cycle is obtained by the rapid insertion of the Th-H moiety of complex [A] into the –C=N–Bpin bong giving rise to intermediate [C] instantly, as this C=N bond is highly activated by the borane moiety (no imine product is detected). The reaction of complex [C] with HBpin, via a Th-N/H-Bpin σ-bond metathesis through the transition state {[C]-[A]}$^{\#}$ produced as the rate determining step the target dihydroborated amine product, and concurrently regenerates the active complex [A] to complete the full catalytic cycle. Since this final hydroboration step is the turnover-limiting step, we cannot eliminate a rapid nitrile coordination equilibrium giving the intermediate [C′].





Scheme 3 Proposed mechanism of hydroboration of nitriles.

Mechanistic Studies for Imine hydroboration. To gain a deeper understanding of the imine hydroboration catalytic cycle and in the activation pathways of complex **Th2**, stoichiometric kinetic and temperature dependence measurements were performed. Stoichiometric reactions between **Th2** and variable ratios of the imine (PhC=NPh), starting from 1 equiv to 5 equiv (Figure S79), at room temperature or at 80 ^{o}C, demonstrated that the complex **Th2**, by itself, does not react with the imine. In addition, in the ^{1}H NMR spectra of the reaction mixture of **Th2** and HBpin (1 – 10 equiv) at room temperature; no reaction is observed. However, after heating the same reaction mixture to 80 ^{o}C for 6 h, two new signals were found at δ 1.02 and 0.33 ppm, corresponding to the formation of pinB–N(SiMe$_3$)$_2$ (Figure S80–S82).[20c]

All our attempts to find and characterize the corresponding hydride or deuteride were not successful, indicating a rapid exchange equilibrium between the hydride at the metal and at the HBpin resulting in an additional fine splitting at the hydride signals of the HBPin that are split by the boron.

Stoichiometric reactions of **Th2**, imine (PhC=NPh) and HBpin (1:5:5) at 80 ^{o}C give directly the hydroborated product and one equiv of PinB–N(SiMe$_3$)$_2$ (Figure S83). Kinetic measurements indicate that the empirical rate law, observed for the hydroboration of PhC=NPh catalyzed by complex **Th2** exhibits a first-order dependence on the catalyst, HBpin and no dependence on imine concentration (Eq. 2) (Figures 3a-c). A thorough analysis of the kinetic equation can be found in the Supporting Information (SI).

$$\delta p/\delta t = k_{obs} \times [\mathbf{Th2}]^1\ [\mathrm{HBpin}]^1\ [\mathrm{PhC{=}NPh}]^0 \qquad (2)$$

Activation parameters for the hydroboration of PhC=NPh were determined from the Eyring and Arrhenius plots with ΔS‡, ΔH‡, and Ea values of −36.46 (0.8) e.u., 13.42 (1.06) kcal/mol and 14.05 (0.77) kcal/mol, respectively (Figures 3d, S102–104). The ΔH‡ and ΔS‡ data are consistent with a concerted bond-cleavage and bond-formation processes and with a very organized four-centered transition state, respectively.

Deuterium isotope studies show that the reaction exhibits a KIE (k_H/k_D) of 2.85 (0.07) (Figure S101), indicating that the Th-N(SiMe$_3$)$_2$/H-Bpin σ-bond metathesis is the operative turnover-limiting step.

Based on these studies, a plausible hydroboration mechanism is proposed for the reaction of **Th2** with PhCH=NPh and HBPin, in Scheme 4. The activation of the reaction cycle is firstly achieved by the Th-N(SiMe$_3$)$_2$/H-Bpin σ-bond metathesis forming the elusive intermediate [A′] through the transition state {[**Th2**]-[A′]}‡. It is important to mention that since no hydride singlet (Th-H) was detected in the ^{1}H NMR, neither in the exchange magnetization transfer ^{2}D experiments, we cannot discard, at least theoretically and to some extent that the complex [**Th2**] and [A′] are in equilibrium. The rapid equilibrium reaction of [A′] with the –C=N- bond of the imine affords the intermediate [B′], that reacts with an additional molecule of HBpin, via a subsequent Th-N/H-Bpin σ-bond metathesis, producing the target hydroborated secondary amine product, and simultaneously regenerating the active species [A′] to complete the catalytic cycle.

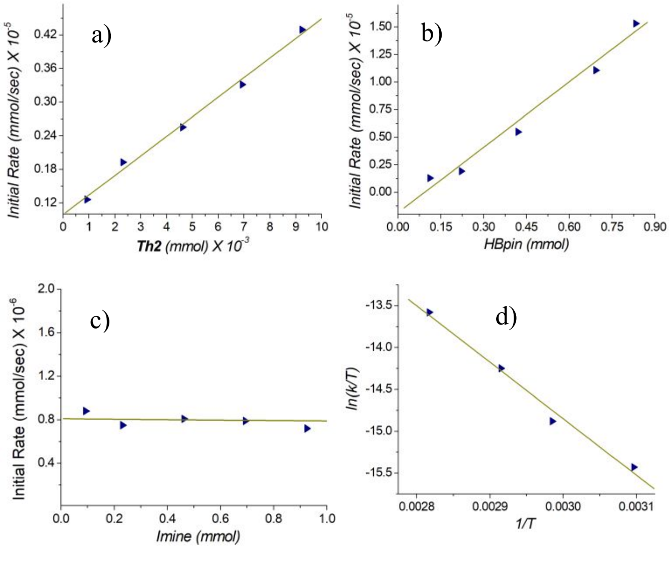
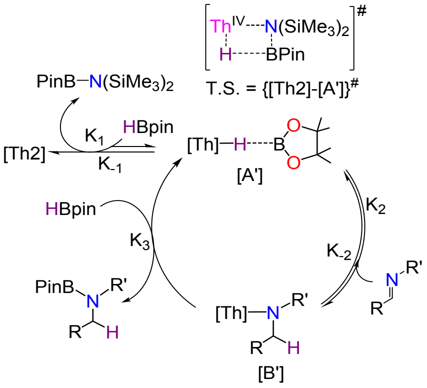


Figure 3 Plot of the initial reaction rate δp⁄δt against the concentration of a) **Th2**, b) HBpin, c) PhC=NPh for the reaction of PhC=NPh and HBpin catalysed by **Th2**; d) Eyring plot of ln(k/T) vs 1/T for the reaction of PhC=NPh and HBpin catalysed by **Th2**.



Scheme 4 Proposed mechanism of hydroboration of imines.

Conclusions

In conclusion, the rapid hydroboration of nitriles with HBpin to the corresponding dihydroborated amines (pro-primary amines) promoted by the thorium amide complex (**Th1**) has been established. **Th1** was found to be a highly effective and versatile precatalyst with a broad substrate scope and according to our knowledge, it displayed the highest TOF among all the catalysts reported in the literature. In addition, the N-heterocyclic iminato thorium complex (**Th2**) was found as an excellent catalyst for the hydroboration of aldimines with HBpin to give the hydroborated amines (pre-secondary amines). Further investigation is dedicated towards the modification of the complex **Th2** to extend his application to ketimines. Efforts to explore chiral counterpart of **Th2** are also underway for asymmetric imine hydroboration and will be reported in due course.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, characterization data, kinetics, thermodynamic data, labeling experiments, Crystallographic Data and Pertinent Refinement Parameters for the complex **Th2**.

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