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Efficient and chemoselective hydroboration of organic nitriles promoted by Ti^{IV} catalyst supported by unsymmetrical acenaphthenequinonediimine ligand

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ABSTRACT

We report the synthesis, characterization, and utilization of a titanium (IV) complex $[(\eta^5\text{-}C_5H_5)\{L\}TiCl_2]$ (**1**) supported by a monoanionic ligand (L), *N*-(2, 6-diisopropyl)acenaphthenequinonediimido, as a molecular pre-catalyst for the hydroboration of nitriles. The unsymmetrical N-silylated *N*-(2, 6-diisopropyl)-*N*-(trimethylsilyl)-acenaphthenequinonediimine ligand (**$LSiMe_3$**) was obtained upon the completion of a one-pot reaction between N-(2, 6-diisopropyl)iminoacenaphthenone and lithium hexamethyldisilazide in the presence of trimethylsilyl chloride in 1:1:1 M ratio at 90 °C. The reaction of $LSiMe_3$ with $\{\eta^5\text{-}(C_5H_5)TiCl_3\}$ in equal proportion (1:1) at 60 °C afforded the titanium complex $[(\eta^5\text{-}C_5H_5)\{L\}TiCl_2]$ (**1**) in good yield. The molecular structures of the N-silyl ligand ($LSiMe_3$) and Ti(IV) complex **1** were established by single-crystal X-ray analysis. Complex **1** was tested as a pre-catalyst for hydroboration of nitriles with pinacolborane (HBpin) and catecholborane (HBcat) to afford diboryl amines at ambient temperature. Titanium complex **1** exhibited high conversion, superior selectivity, and broad functional group tolerance during hydroboration of nitriles with both HBpin and HBcat under mild conditions.

1. Introduction

Recent trends in synthetic chemistry demonstrate the growth in use of synthetic methods in multicomponent reactions and catalysis using earth-abundant metals. Multicomponent reactions emphasize the progress of reactions using fewer (compared to conventional reactions) steps, while the choice of earth-abundant metals is driven by non-toxicity and economy of cost. Titanium is the second-most abundant metal on earth and is also non-toxic. It has therefore been used as a preeminent catalyst in several important multicomponent reactions [1]. Besides its use as a catalyst in synthetic organic and inorganic chemistry, titanium has seen widespread application in biomedicine [2], nanochemistry [3], aerospace [4], and other interdisciplinary areas [5]. Titanium has also been an essential metal catalyst for diverse synthetic reactions such as asymmetric epoxidation [6], polymerization [7], and coupling reactions [8]. Amongst titanium metal precursors, cyclopentadienyl-supported Ti^{IV} complexes have been important reagents for a long time. In the present day, they have emerged as vital components in several organic transformations [9]. Nevertheless, the use of titanium complexes in the synthesis of organoboron compounds has not been explored, although a wide range of transition metals have been found to act as efficient catalysts in the hydroboration of unsaturated compounds (Fig. 1).

Organoboron compounds are applied widely – in pharmaceuticals [10], agrochemicals [11], synthesis of natural products [12], material synthesis, as well as several organic transformations [13]. Hydroboration of unsaturated compounds such as alkenes [14], alkynes [15], and carbonyl compounds [16] has been widely practiced, as it provides many simple and useful precursors for organic reactions. Synthetic chemists find it advantageous to use organoboron compounds because of they are easy to handle and are atom efficient. However, hydroboration of nitriles is more resource rich, since the resultant free amines are beneficial for many industrial processes [17]. Over the past few years, numerous methods have been reported, including with the use of transition metals and alkaline metals (Fig. 1). Ruthenium(II)-based metal complexes were used as efficient catalysts by Gunanathan et al. and Szymczak et al. for the hydroboration of nitriles and imines for the synthesis of diboryl amines [18]. A Fe–In complex was reported by the Nakazawa working group in the efficient hydroboration of both aryl and

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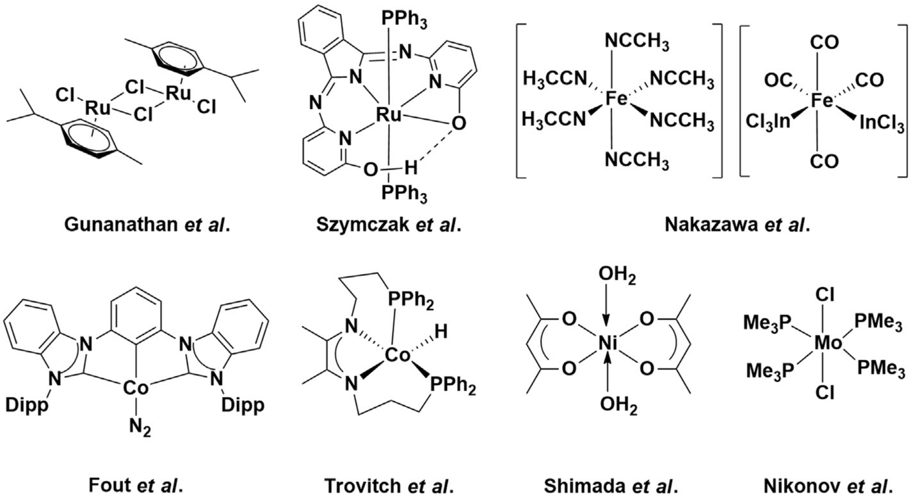


Fig. 1. Selected transition metal catalysts for hydroboration of nitriles.

alkyl nitriles [19]. Transition metal−based complexes such as Co(I) [20], Co(II) [21], and Ni(II) [22] have also been reported in nitrile hydroboration by both pinacolborane (HBpin) and catecholborane (HBcat) by the Fout, Trovitch, and Shimada groups respectively.

Nikonov and colleagues demonstrated the hydroboration of acetonitrile and benzonitrile by HBcat, catalyzed by molybdenum(IV) [23]. Further, Mg(II) complex was reported by Hill et al. as the only alkaline earth metal known till date for nitrile hydroboration [24]. Very recently, the Eisen working group demonstrated the use of Th(IV)-amide metal catalysts in the rapid hydroboration of nitriles and imines [25].

Therefore, in recent years, synthetic chemists have frequently used less toxic earth-abundant metal catalysts in novel catalytic reactions under mild conditions. Our research group has conducted hydroboration reactions on carbonyl compounds using efficient alkali metal catalysts [26]. Very recently, our group also reported the chemoselective hydroboration of an organic nitrile with an earth-abundant aluminum alkyl metal complex [27]. This motivated us to conduct further research into the efficient hydroboration of organic nitriles by a titanium-based metal complex.

In this paper, we report the synthesis as well as structural aspects of a titanium(IV) complex of *N*-(2, 6-diisopropylphenyl)-acenaphthenequinonediimido ligand, which was further tested as an efficient catalyst for the chemoselective hydroboration of a large array of nitriles by HBpin and HBcat under mild conditions.

2. Experimental section

2.1. Materials

All manipulations involving air- and moisture-sensitive compounds were carried out with argon, using the standard Schlenk technique or argon-filled MBraun glove box. $CDCl_3$ and C_6D_6 were distilled and stored in the glove box. ^{1}H NMR (400 MHz), ^{13}C{1H} NMR (100 MHz), and ^{11}B{1H} (128 MHz) spectra were measured on a BRUKER AVANCE III-400 spectrometer. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer at 298 K in $CDCl_3$, and chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to internal standard tetramethylsilane (TMS) ($\delta_H = 0.00$ ppm). ^{13}C{1H} NMR spectra were recorded on a 100 MHz spectrometer at 298 K in $CDCl_3$, and chemical shifts (δ ppm) are reported relative to $CHCl_3$ [$\delta_C = 77.00$ ppm (central line of the triplet)]. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Hydrocarbon solvents (*n*-hexane, toluene) were distilled in nitrogen atmosphere from sodium benzophenone and $LiAlH_4$ and stored inside the glove box. All the starting materials − acenapthequinone, 2,6-diisopropylaniline, lithium bis(-trimethylsilyl)amide, trimethylsilyl chloride, (cyclopentadienyl) titanium trichloride, and organic nitriles − were purchased from Sigma Aldrich India and used without further purification. HBpin and HBcat were purchased from Sigma Aldrich India and distilled prior to use. The ligand N-(2, 6-diisopropyl)iminoacenaphthenone was prepared in accordance with methods reported in literature [28].

2.2. Synthesis of N-(2, 6-diisopropyl)-N-(trimethylsilyl)-acenaphthenequinonediimine (**LSiMe₃**)

N-(2, 6-diisopropyl)iminoacenaphthenone (1.0 g, 0.003 mmol) and $Li(NSiMe_3)_2$ (0.490 g, 0.003 mmol) were taken in a dried 25 ml Schlenk tube inside the glove box, and 5 ml toluene was added. The reaction mixture was stirred for 2 h. Trimethylsilyl chloride (0.37 ml, 0.003 mmol) was then added to the reaction mixture under inert conditions and heated for 18 h at 90 °C. During the course of the reaction, a yellow precipitate was observed. The resulting solution was evaporated under reduced pressure to afford a solid yellow residue. The solid product was extracted from hexane (3 × 15 ml) under inert conditions. The ligand $LSiMe_3$ was obtained as a yellow crystalline product after removing the solvent under reduced pressure, and was further purified by recrystallization from toluene at −35 °C.

Yield: 1.0 g, 83%. FT-IR (selected frequency in cm^{-1}): $\nu = 2961$ (*sp³* C−H str.), 1625 (C═N str.), 1585, 1460, 1435 (aromatic C═C str.), 849 (C−H deforming), 1322 (*sp³* C−H bending). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, *J* = 8.0 Hz, 1H, Ar−*H*), 7.86 (d, *J* = 8.0 Hz, 1H, Ar−*H*), 7.79 (d, *J* = 8.0 Hz, 1H, Ar−*H*), 7.62 (t, *J* = 8.0 Hz, 1H, Ar−*H*), 7.23−7.14 (m, 4H, Ar−*H*), 6.42 (d, *J* = 4.0 Hz, 1H, Ar−*H*), 2.80−2.69 (sept, 2H, C*H*), 1.08 (d, *J* = 8.0 Hz, 6H, CH_3), 0.77 (d, *J* = 8.0 Hz, 6H, CH_3), 0.36 (s, 9H, Si(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 166.5 (Ar *C*═*N*), 159.3 (Si *C*═*N*), 146.8, 141.9, 137.7 (d, *J* = 57.0 Hz), 130.9, 129.0 (d, *J* = 64.0 Hz), 127.8 (d, *J* = 76.0 Hz), 124.0 (d, *J* = 55.0 Hz), 122.9, 119.0, 28.0 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 1.4 ($Si(CH_3)_3$) ppm. Elem. anal. Calcd for $C_{27}H_{32}N_2Si$ (412.64 g mol^{-1}): C, 78.59; H, 7.82; N, 6.79. Found: C, 78.33; H, 7.41; N, 6.52.

2.3. Synthesis of **[(η^5-C_5H_5){L}$TiCl_2$] (1)**

To a solution of **LSiMe$_3$** (200 mg, 0.485 mmol) in toluene (15 ml), (cyclopentadienyl)titanium trichloride (106 mg, 0.485 mmol) was added and the reaction mixture was heated for 12 h at 60 °C. The yellow solution gradually turned dark red. The resulting solution was then evaporated under reduced pressure to give a dark red solid residue. This residue was further purified by washing with cold hexane and recrystallized from a toluene/*n*-pentane mixture (4:1) at −35 °C to give red crystals.

Yield: 229 mg, 88%. ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.43 (d, *J* = 8.0 Hz, 1H, Ar−*H*), 7.10 (d, *J* = 8.0 Hz, 2H, Ar−*H*), 7.03–7.01 (m, 1H, Ar−*H*), 6.94 (t, *J* = 4.0 Hz, 2H, C*H*$_3$), 6.87–6.80 (m, 3H, Ar−*H*), 6.49–6.47 (m, 2H, Ar−*H*), 6.15 (s, 5H, Cp-*H*), 2.80–2.70 (sept, 2H, C*H*), 0.94 (d, *J* = 4.0 Hz, 6H, C*H*$_3$), 0.67 (d, *J* = 8.0 Hz, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 160.8 (Ar *C*═*N*), 148.1 (Si *C*═*N*), 141.9, 136.0 (d, *J* = 87.0 Hz), 131.6, 130.6, 129.4 (d, *J* = 36.0 Hz), 125.6, 124.1 (d, *J* = 26.0 Hz), 122.8, 119.7, 118.3 (Cp-*C*), 29.2 (*C*H(CH$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$) ppm. Elem. anal. Calcd for $C_{30}H_{31}N_2Cl_2Ti$ (538.35): C, 66.93; H, 5.80; N, 5.20. Found: C, 66.65; H, 5.44; N, 4.96.

2.4. General procedure for catalytic hydroboration of organic nitriles to diboryl amines from HBpin (**2a–2s**)

Catalyst **1** (10 mol%) and HBpin (0.44 mmol) were added to a Schlenk flask inside the glove box, followed by the addition of organic nitriles (0.2 mmol). The reaction mixture was heated continuously at 65 °C under neat condition or under toluene for a stipulated time, as mentioned in Table 2. Toluene was then added, and the reaction mixture was filtered through a short plug of Celite and evaporated under reduced pressure to obtain a solid residue. The diboryl amines are moisture- and air-sensitive, and hence experimental procedures were conducted and NMR samples were prepared inside the glove box. All products were characterized using multi-nuclear NMR spectroscopy, and details are given in the supporting information.

Table 1
Single crystal data and structure refinement parameters for **LSiMe$_3$** and **1**.

Compound	LSiMe$_3$	1
CCDC No.	1941996	1941995
Formula	$C_{27}H_{32}N_2Si$	$C_{29}H_{28}N_2Cl_2Ti$
Formula weight	412.63	523.33
Temperature(K)	293(2)	150(2)
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	11.7251(9)	11.2164(16)
b (Å)	13.0093(9)	11.3860(2)
c (Å)	17.3664(14)	11.8302(16)
α (°)	79.035(7)	73.364(14)
β (°)	79.131(7)	61.820(14)
γ (°)	79.251(6)	84.315(14)
Z	4	2
Volume A [3]	2522.6(3)	1274.8(4)
d_{calc} (g cm-3)	1.086	1.363
μ(mm-1)	1.108	4.919
2θ range (°)	1.614–25.817	4.056–70.656
Total Reflections	18963	8067
Unique Reflections	9465	4596
Observed data[I > 2σ(I)]	9465	4596
No. of parameters	555	311
R(int)	0.0433	0.0631
R_1 [I > 2 σ (I)]	0.0688	0.0513
R1, w*R*2 (all data)	0.1090, 0.2204	0.0851, 0.1226
GooF (all data)	1.286	1.003
Max. peak/hole	0.131/-0.268	0.321/-0.338

2.5. General procedure for catalytic hydroboration of organic nitriles to diboryl amines from HBcat (**3a–3m**)

Catalyst **1** (10 mol%) and catecholborane (0.44 mmol) were added to a Schlenk flask inside the glove box, followed by organic nitriles (0.2 mmol). The reaction mixture was heated continuously at 65 °C under neat condition or under toluene for a stipulated time, as mentioned in Table 2. The progress of the reaction was monitored by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (50 mol%) as an internal standard.

2.6. X-ray crystallography

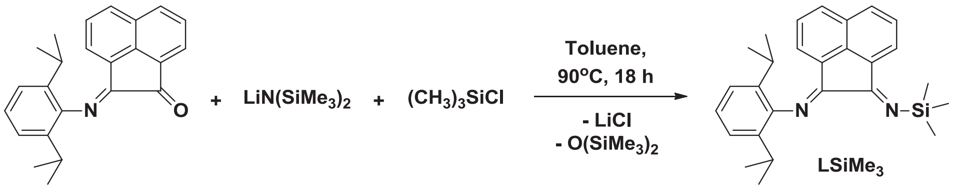
The X-ray data of **LSiMe$_3$** and catalyst **1** were collected in an Agilent Supernova X-Calibur Eos CCD detector with graphite-monochromatic Mo-Kα (0.71073 Å) (**LSiMe$_3$)** or Cu-Kα (1.54184 Å) (**1**) radiation, either at room temperature (**LSiMe$_3$)** or at 150 K (**1**). The structures of both were solved by direct methods (SIR2004) [29] and refined on *F* [2] by full-matrix least-squares methods using SHELXL-2016/6 [30]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma$ [2](F_o^2) + (aP) [2] + bP]), where P = (Max(F_o^2,0) + 2F_c^2)/3 with σ [2](F_o^2) from counting statistics. The function *R*1 and w*R*2 were $(\sigma||F_o|-|F_c||)/\sigma|F_o|$ and $[\sigma w(F_o^2-F_c^2)^2/\sigma(wF_o^4)]^{1/2}$ respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1941995 (**1**) and 1941996 (**LSiMe$_3$**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk). The crystal data are displayed in Table 1.

3. Results and discussion

3.1. Synthesis and structures

The unsymmetrical *N*-(2, 6-diisopropyl)-*N*-(trimethylsilyl)-acenaphthenequinonediimine (**LSiMe$_3$**) ligand was readily prepared, yielding 83% of a highly pure product, by the one-pot reaction between N-(2, 6-diisopropyl)iminoacenaphthenone and anhydrous lithium hexamethyldisilazide in toluene, followed by the addition of trimethylsilyl chloride in equimolar (1:1:1) ratio at 90 °C (Scheme 1).

The nucleophilic reaction of hexamethyldisilazide occurs at the carbonyl carbon center of N-(2, 6-diisopropyl)iminoacenaphthenone, followed by rearrangement of −N(SiMe$_3$)$_2$ group and elimination of lithium chloride and hexamethyldisiloxane, affording the desired product, i.e. **LSiMe$_3$**. In the ^{1}H NMR spectrum of **LSiMe$_3$**, the signal for the amine Si(C*H*$_3$)$_3$ hydrogen atoms appears as a singlet at $\delta_H = 0.36$ ppm. The resonance of the isopropyl C*H*$_3$ protons appears as two doublets, at $\delta_H = 0.77$ ppm and 1.08 ppm. The methine proton (CH) of the ligand appear at $\delta_H = 2.74$ ppm as a septate signal. The solid-state structure of **LSiMe$_3$** was established by single-crystal X-ray diffraction. Its molecular structure is depicted in Fig. 2. **LSiMe$_3$** crystallizes in the triclinic space group *P*-1 with four molecules in the unit cell. Details of the structural and refinement parameters of the crystal structure of **LSiMe$_3$** are given in Table 1. The N−Si bond distance of 1.740(4) Å in **LSiMe$_3$** is very similar to that previously reported for 1,2-bis[(trimethylsilyl)imino]acenaphthene−supported complexes (1.791–1.797 Å) [28a]. The C1−N1 bond distance of 1.261(5) Å is consistent with distances measured in other *N,N'*-(bisaryl)acenaphthenequinonediimine ligands, and is hence indicative of N═C double bonds [28a].



Scheme 1. Synthesis of *N*-silyl ligand **LSiMe$_3$**.

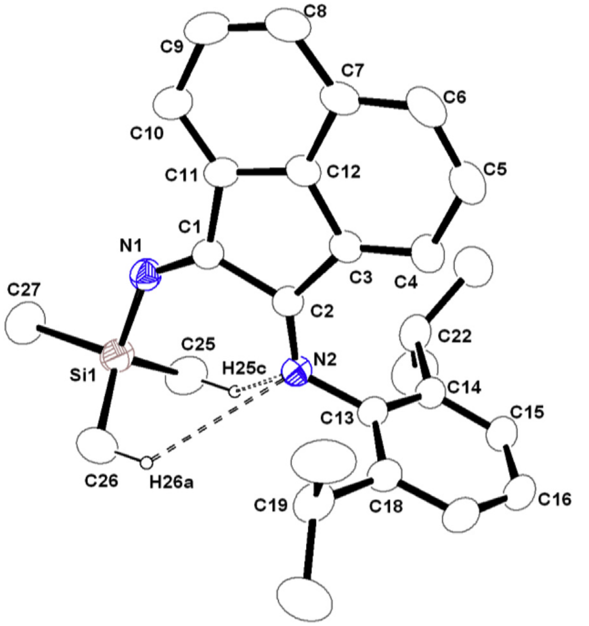


Fig. 2. The molecular solid-state structure of the *N*-silyl ligand, **LSiMe$_3$**.
Hydrogen atoms except 25c and 26a are omitted for clarity. Selected bond lengths (Å) and angles (°): C1–N1 1.261(5), N1–Si1 1.740(4), C2–N2 1.270(5), N2–C13 1.432(5), C1–C2 1.538(6), C1–N1–Si1 136.4(3), C1–C2–N2 121.1(4), C2–N2–C13 119.8(4).

Further reaction of **LSiMe$_3$** with *η*^{5} -cyclopentadienyl titanium(IV) trichloride [(η^5 -C$_5$H$_5$)TiCl$_3$] in toluene at 60 °C resulted in the formation of a corresponding mixed ligand titanium complex [(η^5 -C$_5$H$_5$){L}TiCl$_2$] (**1**) in 88% yield, through elimination of the volatile trimethylsilyl chloride (Scheme 2). Titanium complex **1** demonstrated good solubility in common organic solvents such as THF and toluene and was characterized using standard spectroscopic and analytical techniques. The solid-state structure of compound **1** was also established by single-crystal X-ray diffraction analysis. In the ^{1}H spectrum of titanium complex **1** measured in C$_6$D$_6$, the cyclopentadienyl $C_5H_5^-$ hydrogen atoms can be seen at $\delta_H = 6.15$ ppm as a sharp singlet. Two doublet (at $\delta_H = 0.67$ ppm and 0.94 ppm) and one septate (at $\delta_H = 2.75$ ppm) resonance signals confirm the presence of isopropyl groups of the ligand moiety **L**.

X-ray quality air- and moisture-sensitive crystals of complex **1** were grown at −35 °C from a concentrated toluene solution. The solid-state structure of complex **1** was determined by single crystal x-ray diffraction analysis. Details of the structural and refinement parameters of the crystal structure of complex **1** are given in Table 1 and molecular structure of complex **1** is shown in Fig. 3. Complex **1** crystallizes in the triclinic space group *P*-1 and has two independent molecules in the unit cell. The molecular structure of Ti(IV) complex (**1**) confirms the attachment of the *N*-(2, 6-diisopropyl) acenaphthenequinonediiminato ligand to the titanium center. Complex **1** is monomeric and the coordination polyhedron is formed by the *κ*^{1} chelation of one iminato nitrogen atom of monoanionic ligand **L**, η^5 -coordination of one cyclopentadienyl moiety,

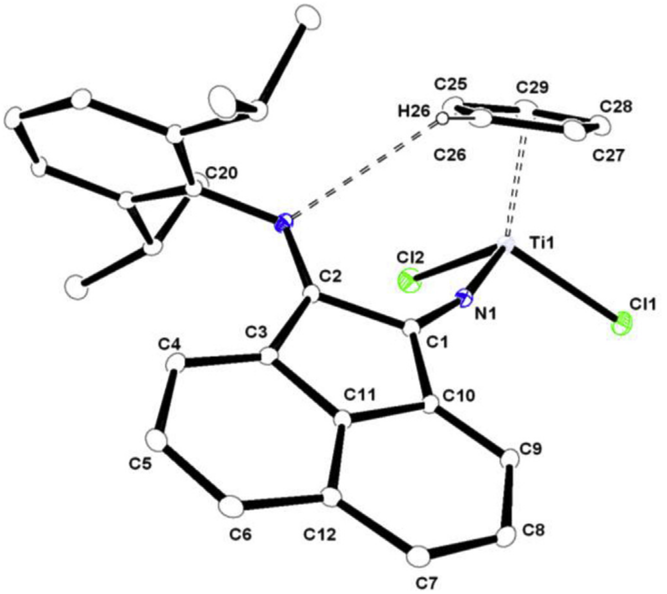
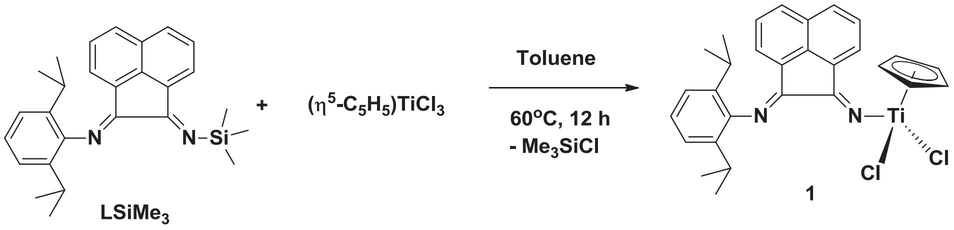


Fig. 3. Representation of the molecular solid-state structure of [(η [5]-C$_5$H$_5$){L}TiCl$_2$] (**1**).
All hydrogen atoms (except H26) are omitted for clarity. Selected bond lengths (Å): Ti1–N1 1.854(3), Ti1–Cl1 2.2817(13), Ti1–Cl2 2.2529(14), Ti1–C25 2.329(4), Ti1–C26 2.341(4), Ti1–C27 2.349(4), Ti1–C28 2.362(4), Ti1–C29 2.362(4), C1–N1 1.260(4), C2–N2 1.275(5), C1–C2 1.534(5), C1–C2–N2 119.9(3), C2–N2–C13 118.4(3), C2–C1–N1 125.5(3), C1–N1–Ti1 163.4(3), N1–Ti1–Cl1 104.91(10), N1–Ti1–Cl2 103.60(10), Cl1–Ti1–Cl2 101.86(5).



Scheme 2. Synthesis of titanium (IV) complex **1**.

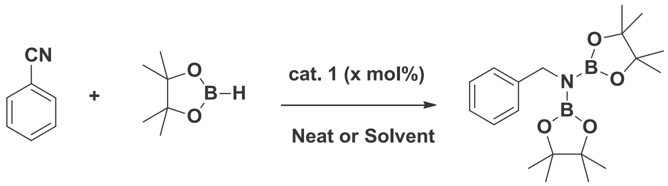
and two chloride ions. The monoanionic iminato ligand **L** was initiated by the elimination of trimethylsilyl chloride (Scheme 2) and thus readily bonded to the Ti center to form the Ti(IV) metal complex **1** in a monodentate fashion. This monodentate coordination of the ligand L to the Ti^{IV} ion is presumably due to the presence of the cyclopentadienyl ring which may prevent the bidentate coordination due to steric factor. The geometry around the titanium ion may best be described as pseudo tetrahedral, in view of the η^5 -$C_5H_5^-$ ring being a pseudo-monodentate ligand. The Ti—N distance [1.854(3) Å] is close to the $Ti\text{-}N_{iminato}$ distance [1.765 (3) Å] and [1.824(2) Å] observed in iminazolin-2-iminato complexes $[(Im^{tBu}N)Ti(\eta^5\text{-Cp})Cl_2]$ [31] and $[(Im^{tBu}N)Ti(NMe_2)_3]$ [32] (Im^RN = Imidazolin-2-iminato) complexes respectively. However, this distance is much shorter than Ti—N covalent bond observed in literature (1.928(2) Å in $[\eta^5\text{-CpTi}((Dipp)_2DAD)Cl]$) [33]. The iminato nitrogen of ligand **L** coordinates to the titanium ion nearly in linear fashion [Ti—N1—C1 = 163.4(3)°]. The Ti—C(Cp) distances, ranging from 2.329(4) to 2.362(4) Å, are in agreement with previously reported Ti—C(Cp) values [31].

3.2. *Catalysis*

3.2.1. *Hydroboration of nitriles with HBpin*

At the beginning of our study, we chose the model reaction condition: 5 mol% of the Ti complex for the hydroboration of benzonitrile and HBpin (2.2 equivalents) at 65 °C, under neat condition. When carried out at room temperature, the reaction yielded 48% of the corresponding diboryl amine product (Table 2, entry 2). We were, however, delighted to observe that complex **1** exhibited good catalytic activity toward the hydroboration of benzonitrile when heated to a temperature of 65 °C, yielding 61% of the product, in the formation of the corresponding boryl amine (Table 2, entry 3). With a higher catalyst loading — up to 10 mol% — under neat condition at 65 °C for 12 h, the desired product was obtained with a yield of 99% (Table 2, entry 4). In addition, we screened the hydroboration reaction separately with no catalyst loading (Table 2, entry 1) and using catalyst at room temperature (Table 2, entry 2). In both cases, we observed no product formation. The efficacy of the catalyst was examined with solvents such as toluene and THF. We observed that toluene produced a good yield — 90% — while THF produced a drastic decrease in yield — 50% of the product (Table 2, entries 5–6). Thus, with a temperature of 65 °C and neat condition, we set out to examine the scope of substrates of various aryl and alkyl nitriles and HBpin in the presence of 10 mol % of the titanium catalyst **1**. Results of the catalytic hydroboration reaction are set out in Table 3.

Table 2
Catalyst screening for hydroboration of benzonitrile with HBpin.



Entry	Catalyst loading (mol%)	Time (h)	T (°C)	Solvent	Isolated yield[a] (%)
1	–	12	65	neat	0
2	5	12	r.t	neat	48
3	5	12	65	neat	61
4	10	12	65	neat	99
5	10	12	65	Toluene	91
6	10	12	65	THF	50

Reaction conditions: catalyst (x mol%), benzonitrile (1 eq.), HBpin (2.2 eq.). The reaction mixture was heated to 65 °C. [a]Isolated yield.

With the optimized condition as the benchmark for the hydroboration reaction with unsubstituted benzonitrile, which afforded a yield of 99% (Table 3, entry 2a), we employed a range of aryl nitriles possessing electron-withdrawing and electron-donating groups, as well as heterocyclic nitriles and aliphatic nitriles, for hydroboration with HBpin. The reactions were smooth in all cases and the results are set out in Table 3. The reaction between HBpin and 4-fluoro, 4-chloro, and 4-bromo benzonitrile afforded a near-quantitative yields of 98%, 96%, and 91% of the diboryl product respectively (Table 3, entries 2b–2d). The reaction of substituted 4-trifluoromethyl benzonitrile with HBpin also afforded an excellent yield of 93% (Table 3, entry 2e) under optimal conditions. The reaction protocol was also found to be very effective for benzonitriles with electron-donating groups under optimized conditions. 4-Methylbenzonitrile produced a quantitative yield of 98% while 4-(tert-butyl)benzonitrile afforded a slightly lower yield of 87% (Table 3, entries 2f–2g). 4-Methoxy, 4-(methylthio), and 4-dimethylamino benzonitrile also provided the diboryl product in good yields — 89%, 82%, and 85% respectively (Table 3, entries 2h–2j).

Additionally, we obtained good yields (up to 80%) from the hydroboration reaction of 1-napthonitrile, picolinonitrile, and thiophene-2-carbonitrile (Table 3, entries 2k–2m). The scope of hydroboration was also extended to 4-(fluorophenyl)acetonitrile and aliphatic nitriles, such as acetonitrile, chloro-, and methoxy acetonitrile, and good yields of up to 75% were obtained for all the substrates under optimized conditions (Table 3, entries 2n–2q). Additionally, we checked the chemoselectivity of the Ti^{IV} catalyst **1** towards hydroboration of methyl-4-cyanobenzoate and 4-cyanobenzaldehyde. In 4-cyanobenzaldehyde, both aldehyde and nitrile groups underwent smooth reduction under optimum conditions, exhibiting no chemoselectivity of the functional groups (Table 3, entry 2r). However, chemoselective reduction of the nitrile group occurred from methyl-4-cyanobenzoate when 2.2 equivalent HBpin was used, keeping the ester group intact (Table 3, entry 2s).

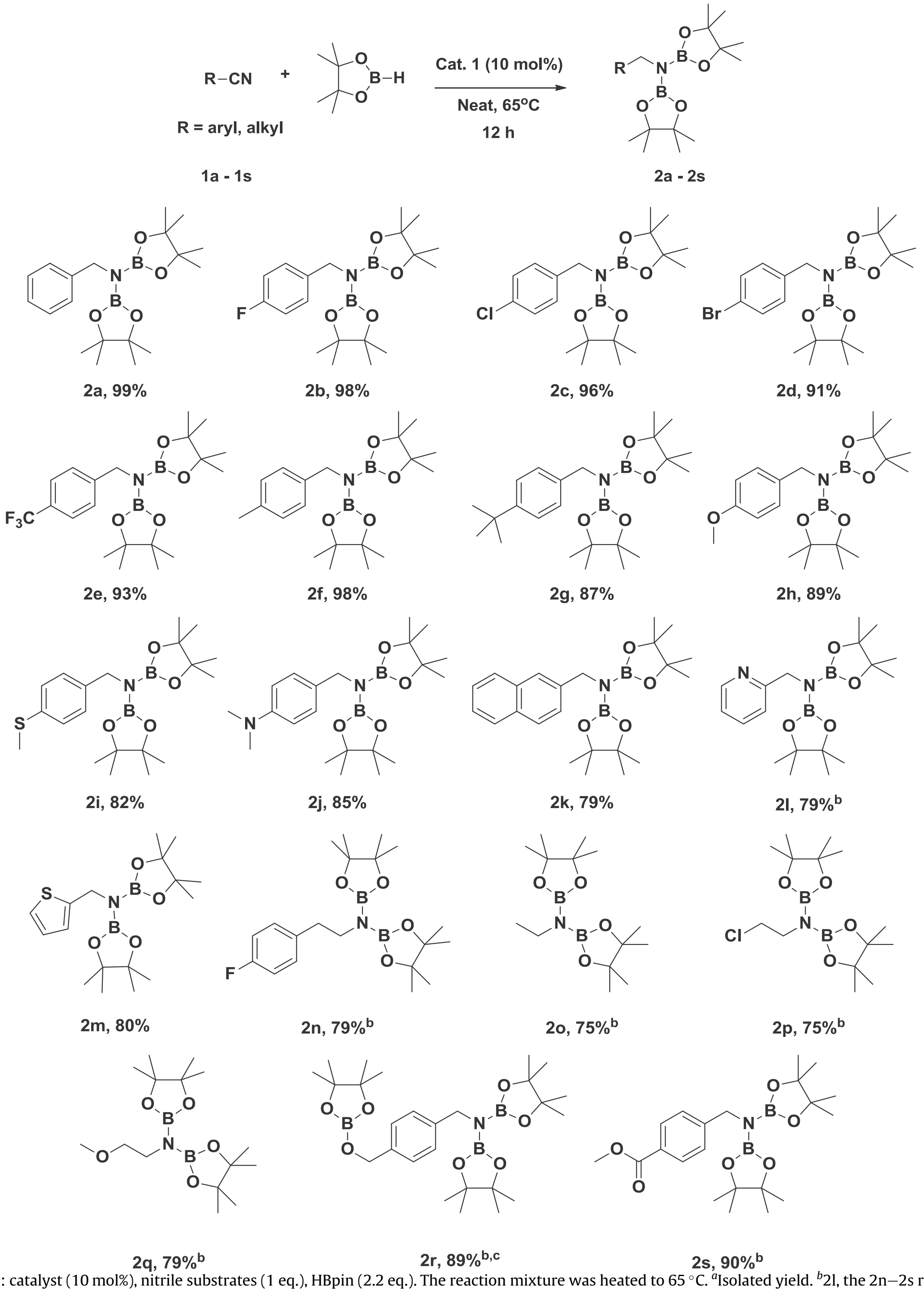
3.2.2. *Hydroboration of nitriles with HBcat*

In order to extend the protocol of our reaction, the efficacy of the titanium catalyst **1** was further examined for the hydroboration of nitriles with HBcat. Under the optimized conditions indicated in Table 1, when 10 mol% of complex **1** was used for the reaction of 1 equivalent of benzonitrile with 2.2 equivalent of HBcat under neat condition, an excellent yield of 99% was observed (Table 4, entry 3a).

The yield was calculated from NMR in the presence of 1,3,5-trimethoxybenzene as an internal standard. With this optimized condition, we re-examined the catalyst efficiency of the substrate scope of nitriles with electron-withdrawing and electron-donating groups, as well as heterocyclic and aliphatic nitriles. In the case of electron-withdrawing halogen substitution, the use of 4-fluoro, 4-chloro, and 4-bromo benzonitrile gave excellent yields — 99% each (Table 4, entries 3b–3d). When the substitution was carried out using the 4-trifluoromethyl group, excellent yield was observed which was in accordance with the other halogen functional groups on benzonitrile (Table 4, entry 3e).

Thereafter, efficiency of the catalyst was investigated through electron-donating substitutions on benzonitriles, such as 4-methylbenzonitrile, and a yield of 83% was obtained (Table 4, entry 3f). Surprisingly, when 4-methoxybenzonitrile was reacted with HBcat, we observed an increase (to 99%) in the yield (Table 4, entry 3h), whereas the reaction with 4-methylthiobenzonitrile resulted in a slight decrease in the yield, at 82% (Table 4, entry 3i). Further decrease of yield (75%) was observed when the hydroboration was carried out on 4-dimethylamino benzonitrile (Table 4, entry 3j),

Table 3
Substrate scope of hydroboration of nitriles with HBpin using Ti^{IV} catalyst **1**.



2a, 99% **2b, 98%** **2c, 96%** **2d, 91%**

2e, 93% **2f, 98%** **2g, 87%** **2h, 89%**

2i, 82% **2j, 85%** **2k, 79%** **2l, 79%**[b]

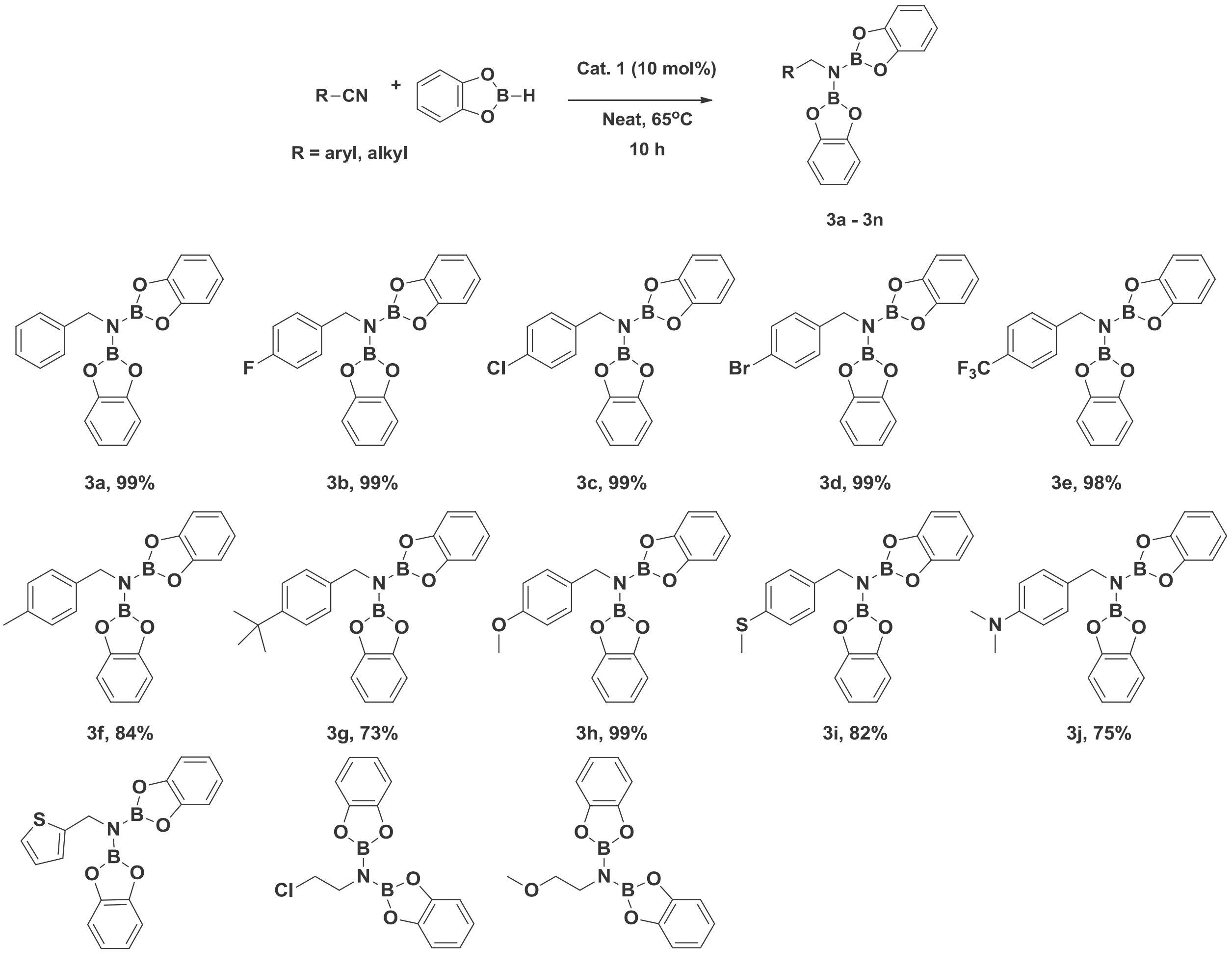
2m, 80% **2n, 79%**[b] **2o, 75%**[b] **2p, 75%**[b]

2q, 79%[b] **2r, 89%**[b,c] **2s, 90%**[b]

Reaction conditions: catalyst (10 mol%), nitrile substrates (1 eq.), HBpin (2.2 eq.). The reaction mixture was heated to 65 °C. [a]Isolated yield. [b]2l, the 2n–2s reaction was carried out in toluene, [c]3 eq. HBpin was used.

probably due to increase in the electron-donating character. It is noteworthy that reaction with the heterocyclic substrate – namely thiophene-2-carbonitrile – again afforded an excellent yield of 99% (Table 4, entry 3k). Hydroboration with HBcat was extended to aliphatic nitriles such as chloro- and methoxy acetonitrile, and excellent yields of up to 95% were obtained for these substrates under optimized conditions (Table 4, entries 3l–3m). The current protocol for hydroboration of nitriles using Ti^{IV} catalyst, is competitive to the existing catalytic system such as Ru [18a], Fe-In [19], Co(I) [20], Co(II) [21], Mo(IV) [23], Mg(II) [24], Th (IV) [25] with respect to substrate scope, yield and reaction time reported by other research groups.

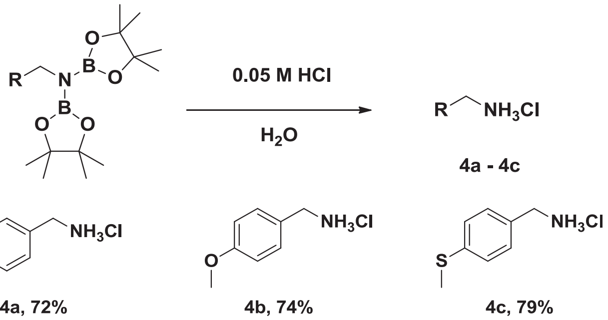
Table 4
The substrate scope of hydroboration of nitriles with HBcat using Ti^{IV} catalyst **1**.



Reaction conditions: catalyst (10 mol%), nitrile substrates (1 eq.), HBcat (2.2 eq.). The reaction mixture was heated at 65 °C. [a]Yields were calculated based on ^1H NMR (400 MHz) integration of characteristic product peak using 50 mol% of 1,3,5-trimethoxybenzene as an internal standard. [b]For **3l**, **3m** the reaction was carried out in toluene.

After the hydroboration of organic nitriles, we performed hydrolysis of diboryl amines for a few substrates to give the corresponding amines. The diborylated amines were treated with 0.05 M aqueous HCl for 4 h at room temperature. The derivatives of benzyl ammonium chloride were obtained as white powder (Table 5, entries 4a–4c) in moderate yields of 70–80%.

Table 5
Hydrolysis of diboryl amines.



For the hydroboration of aryl nitriles with HBpin, the reaction progress with various substrates – ranging from electron-withdrawing to electron-donating and heterocyclic groups – was monitored by in situ ^1H NMR. The reactions were carried out in a screw-cap NMR tube charged with C_6D_6 which were sealed and heated to 65 °C at regular intervals.

The conversion of diboryl products was carried out on 1 equivalent of benzonitrile (**1a**), *p*-tolylbenzonitrile (**1f**), *p*-methoxybenzonitrile (**1h**), *p*-(methylthio)benzonitrile (**1i**), and thiophene-2-carbonitrile (**1m**), each with 2.2 equivalent of HBpin in the presence of the Ti^{IV} catalyst, followed by 1,3,5-trimethoxybenzene (20 mol%) charged with C_6D_6. The characteristic product formation was not observed at room temperature. Thereafter the NMR tubes with the reaction mixture were heated to 65 °C at regular intervals of time, such as 30 min. Although complete conversion of the products was not achieved within 5 h, we observed a gradual increase in the formation of characteristic products – the increase progressed in linear fashion with the passage of time.The most plausible mechanism has been proposed based on previous literature [18a,27]. We propose the formation of titanium hydride [Ti–H] complex (**I**) as the active species through the reaction of catalyst **1** and HBpin. Fig. 4 in ESI describes the proposed mechanism.

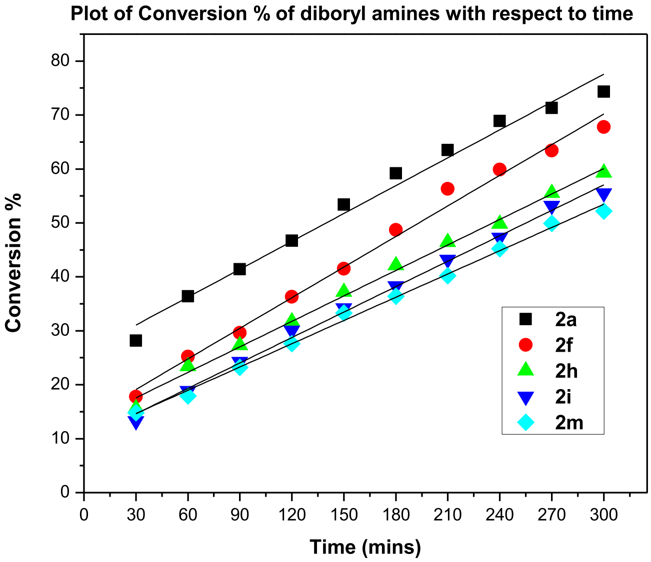


Fig. 4. Reaction progress monitoring by ^{1}H NMR. **1** (0.0095 mmol), nitrile (0.095 mmol), HBpin (0.21 mmol) in a screw-cap NMR tube charged with C_6D_6 and heated to 65 °C at regular intervals. Conversion (%) is determined from ^{1}H NMR integration. 1,3,5-trimethoxybenzene (10 mol%) was used as an internal standard.

4. Conclusions

To summarize, we have reported the synthesis of a titanium (IV) metal complex supported by a monoanionic, *N*-(2, 6-diisopropyl) acenaphthenequinonediiminato ligand. We have also established the molecular structure of the complex. We have utilized Ti^{IV} complex **1** as a pre-catalyst for hydroboration of various aryl and alkyl nitriles with HBpin and HBcat to afford corresponding diboryl amines at ambient temperature. Catalyst **1** has shown a broad substrate scope, ranging from electron-withdrawing to electron-donating groups on aryl and alkyl nitriles, as well as heterocyclic nitriles, producing excellent to good yields. The corresponding primary amines were isolated in good yields for a few substrates. The mechanism involves the formation of a titanium hydride intermediate upon reaction with HBpin, which acts as the active pre-catalyst.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120958.

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