Highly Chemoselective Hydroboration of Alkynes and Nitriles Catalyzed by Group 4 Metal Amidophosphine–Borane Complexes

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ABSTRACT: We report a series of titanium and zirconium complexes supported by dianionic amidophosphine–borane ligands, synthesized by amine elimination and salt metathesis reactions. The TiIV complex [{Ph2P(BH3)N}2C6H4Ti(NMe2)] (1) was obtained by the reaction between tetrakis-(dimethylamido)titanium(IV) and the protic aminophosphine–borane ligand [{Ph2P(BH3)NH}2C6H4] (LH2) at ambient temperature. Both the heteroleptic zirconium complexes [η5-(C5H5)2Zr{Ph2P-(BH3)N}2C6H4] (2) and [{(Ph2P(BH3)N)2C6H4}ZrCl2] (3) and the homoleptic zirconium complex [{(Ph2P(BH3)N)2C6H4}2Zr] (4) were obtained in good yield by the salt metathesis reaction of either zirconocene dichloride [η5-(C5H5)2ZrCl2] or zirconium tetrachloride with the dilithium salt of the ligand [{Ph2P(BH3)NLi}2C6H4] (LLi2), which was prepared in situ. The molecular structures of the complexes 1, 2, and 4 in their solid states were confirmed by single-crystal X-ray diffraction analysis. Of these complexes, only titanium complex 1 acts as an effective catalyst for the facile hydroboration of terminal alkynes, yielding exclusive E-isomers. The hydroboration of organic nitriles yielded diborylamines with a broad substrate scope, including broad functional group compatibility. The mechanism of hydroboration occurs through the formation of titanium hydride as an active species.

INTRODUCTION

Catalytic hydroboration of unsaturated bonds produces organoboron compounds and their derivatives, including vinyl boronates, diborylamines, and boronic esters, which act as powerful synthetic intermediates in various organic and natural product syntheses, as well as the foundation for several chemical transformations in the pharmaceutical industry. Vinyl boronates are effectively used as synthons in organic chemistry, in aldol reactions, in diverse coupling reactions; they are also used as Michael donors. Diborylamines and boronic esters can readily undergo hydrolysis to generate free amines and alcohols, which are essential precursors to the production of polyesters, dyes, and agrochemical as well as pharmaceutical compounds. The main advantage of organoboron compounds is that they are quite stable and easy to handle. Hydroboration reactions are often atom-efficient. Consequently, countless metal-catalyzed and metal-free procedures have been developed to carry out the addition of boranes to unsaturated bonds, such as organic alkynes, alkenes, carbonyl, and nitriles. Several research groups have reported the regioselective and stereoselective hydroboration of alkynes and alkenes to produce vinyl boronates and alkyl boronate, catalyzed by transition metals such as Fe, Co, Cu, Ru, Rh, and Ir. Additionally, there are some reports of hydroboration of carbonyl compounds affording boronic esters, catalyzed by Co, Fe, and Ru. Main-group metal-catalyzed hydroboration of terminal alkynes and organic nitriles is also well reported in the literature. Using commercially available aluminum hydride (iBu2AlH) and LiAlH4 or sodium borohydride (NaBH4) is a well-known means of reduction of alkynes and alkenes, followed by aryl and alkyl nitriles. However, these reagents are combustible and generate large amounts of inorganic waste, which render the process unfavorable. Owing to an increasing trend in adopting the use of earth-abundant metal catalysts in various catalytic reactions, researchers across the world are exploring...
the development of a mild synthetic process catalyzed by earth-abundant metals with a wide substrate scope, possessing good functional group tolerance and occurring within a short reaction time.

Modern chemistry mainly deals with the use of nontoxic and earth-abundant metals that are considered green and sustainable, in addition to being economical and easily available.\(^{30-34}\) Recently, our research group has demonstrated the chemoselective hydroboration of organic nitriles with pinacolborane (HBpin) and catecholborane (HBcat), catalyzed by an alkyl aluminum complex,\(^{35}\) but the scope of the precatalyst was limited. This prompted us to explore the hydroboration of a variety of C–X (X = C, N) multiple bonds, catalyzed by another earth-abundant group 4 metal—titanium.

Although Smith et al. and Hartwig et al. have already reported the titanium-mediated borylation of olefin, such catalytic reactions usually have a very limited substrate scope.\(^{36-38}\) Srebnik et al. have also reported the hydroboration of alkynes with HBpin, catalyzed by zirconocene chloride hydride.\(^{39}\) Our research group has already succeeded in the synthesis of a series of mononuclear and dinuclear titanium complexes bearing a bis(phosphinoselenoic amide) ligand that act as effective catalysts for the hydroelementation of heterocumulenes under mild reaction conditions.\(^{40,41}\) This work induced us to synthesize a new class of aminophosphine–borane ligands and introduce them to group 4 metal chemistry, to utilize the chelating behavior of aminophosphine–borane ligands in homogeneous catalysis and apply it in group 4
metal chemistry. These metal amidophosphine–borane complexes can manipulate their interactions with the metal centers, thus making them very interesting to use in various synthetic protocols.

Here, we report the synthesis of group 4 metal complexes using amidophosphine–borane ligands and explore their catalytic efficiency in the hydroboration of alkynes and nitriles with HBpin under mild conditions to yield the corresponding (E)-alkenyl boranes and diborylamines as exclusive products (Figure 1).

## RESULTS AND DISCUSSION

The preparation of catalysts was carried out using a borane derivative of the amidophosphine ligand (L1-H2), which was synthesized by the reaction between \(N,N’\)-bis(diphenylphosphino)benzene-1,2-diamine [Ph2PNHC6H4NH-PPh2] and dimethyl sulfoxide (diphenylphosphino)-benzene-1,2-diamine \([\text{Ph2P(CH3)N}2C6H4]\) Li2(THF)4 a convenient method, in which the ligand L1-H2 was treated with tetrakis(dimethylamido) titanium(IV) in a 1:1 molar ratio in toluene at room temperature (Scheme 1). In contrast, the reaction of anhydrous zirconocene dichloride \((\text{Cp}_2\text{ZrCl}_2)\) with dianionic lithium salt \([\text{[Ph}_2\text{P(BH}_3)\text{N}2\text{C}_6\text{H}_4\text{Li}_2(\text{THF})}_4]\) afforded the corresponding bis-cyclopentadienyl zirconium complex \((\text{Cp}_2\text{Zr[Ph}_2\text{P(BH}_3)\text{N}2\text{C}_6\text{H}_4]})\) (2) in good yield with the elimination of 2 equiv of lithium chloride (Scheme 1). The heteroleptic zirconium dichloride complex \([\text{[Ph}_2\text{P(BH}_3)\text{N}2\text{C}_6\text{H}_4\text{ZrCl}_2]}\) (3) and homoleptic zirconium complex \([\text{[Ph}_2\text{P(BH}_3)\text{N}2\text{C}_6\text{H}_4\text{Zr}]}\) (4) were isolated in good yield through the one-pot treatment of ligand L1-H2 and lithium bis(trimethylsilylamide) \([\text{Li[N(SiMe}_3]_2}]\) with ZrCl4 in a 2:1:1 and 2:4:1 molar ratio, respectively, in toluene at 70 °C, which also generated LiCl as precipitate (Scheme 1). All of the new Ti and Zr complexes, 1–4, were fully characterized using multinuclear NMR spectroscopy and elemental analyses. The solid-state structures of complexes 1, 2, and 4 were confirmed by single-crystal X-ray diffraction analysis. However, good-quality crystals of complex 3 were not obtained and therefore, the data recorded were poor.

In complexes 1–4, the absence of a resonance signal at \(\delta_H\) 4.84 ppm, assigned to –NH protons for the free ligand, confirmed the formation of fragments of the diamionic ligand L1 [Figures S5, S9, S13, and S17 in the Supporting Information (SI)]. Additionally, the characteristic singlet resonance at \(\delta_H\) 3.21 ppm confirmed the presence of two dimethylamido groups [\(-\text{N(CH}_3)_2\)] in complex 1 and resonances of the cyclopentadienyl protons in complex 3 appeared at \(\delta_H\) 6.00 ppm as a sharp singlet, indicating identical chemical environments for the two cyclopentadienyl rings (Figures S5 and S9 in the SI). Likewise, in the \(^{31}\text{P}[^1\text{H}]\) NMR spectral data, the complexes exhibited sharp signals at \(\delta_P\) 74.1 ppm (complex 1), 69.8 ppm (complex 2), 66.5 ppm (complex 3), and 66.9 (complex 4) ppm, which are fundamentally low-field-shifted when contrasted to the signal of the free ligand L1-H2 (Figures S7, S11, S15, and S19 in the SI).

### Crystal X-ray data and structure refinement parameters for complexes 1, 2, and 4

Single crystals of complexes 1, 2, and 4 were analyzed by X-ray diffraction. The crystals were isolated from the concentrated toluene solution of the corresponding complex at \(-35^\circ\text{C}\). The solid-state structures of the complexes are consistent with their observed solution-phase behavior. The molecular structures of complexes 1, 2, and 4 are shown in Figures 2, 3, and 4, respectively, and the details of the single-crystal X-ray data and structure refinement parameters for complexes 1, 2, and 4 are provided in Table S1 in the Supporting Information. 

Titanium complex 1 crystallizes in the monoclinic space assembly \(P_{2_1}/c\), with four molecules in the unit cell. The coordination polyhedron is formed by the chelation of ligand L1, which is bonded to the TiIV metal ion through two amido nitrogen atoms. Additionally, two dimethylamido groups are attached to the TiIV metal ion (Figures 2, 3, and 4). The solid-state structures of complexes 1, 2, and 4 are shown in Figures 2, 3, and 4, respectively, and the details of the single-crystal X-ray data and structure refinement parameters for complexes 1, 2, and 4 are provided in Table S1 in the Supporting Information. 

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Zirconium complex 2 crystallizes in the triclinic space group \(P1\), with four molecules in the unit cell. Complex 2 is monomeric, and the coordination polyhedron is formed by the chelation of two amido nitrogen atoms of the diamionic ligand L1, along with \(\eta^5\)-coordination of two cyclopentadienyl moieties to the ZrIV ion, adopting a tetrahedral geometry (Figure 3). Since the radius of the Zr(IV) ion is greater than that of the Ti(IV) ion, the Zr–N distances [2.287(19) and...
with the Zr–N covalent bond distances reported in the literature. Both the Zr–C(Cp) distances [Zr1–C39 is 2.527(3) Å and Zr1–C33 is 2.536(3) Å] are within the range of Zr–C(Cp) distances reported for other zirconocene complexes.

The homoleptic zirconium complex 4 crystallizes in the monoclinic space group P2_1/c with four independent molecules in the unit cell. The Zr center is chelated by four amido nitrogen atoms of the two dianionic ligands L1. The geometry around the zirconium ion can be described as a distorted tetrahedral (Figure 4). Similar to complex 1, short distances of 2.324 Å (Zr–H4a) and 2.377 Å (Zr–H3c) are observed between the B–H hydrogen atoms and the ZrIV metal ion, presumably due to crystal packing (Figure 2). However, in the 1H NMR spectra, all of the BH3 protons exhibited at δ_H 1.94 ppm, indicating that all of the borane groups are chemically equivalent in complex 4.

Catalytic Hydroboration of Alkynes and Nitriles. First, the reaction conditions were optimized using phenylacetylene and benzonitrile as model substrates for alkyne hydroboration and nitrile hydroboration, respectively, with HBpin in the presence of all of the catalysts, complexes 1–4. Table 1 contains a summary of all of the results. Control reactions were performed without a catalyst, and we observed no traces of the product (Table 1, entry 1). Initial hydroboration was carried out with 1 mol % loading of complex 1, and it was observed that the reaction of phenylacetylene with 1.1 equiv of HBpin, either in toluene as a solvent or in neat condition, yielded 99% of the (E)-alkenyl borane product (5a) at room temperature in only 1 h (Table 1, entries 2 and 3).

After preliminary evaluation of the catalysts for hydroboration of alkynes, we concluded that titanium catalyst 1 is substantially more efficient than analogs of zirconium complexes (2–4). The labile titanium amido bond in catalyst 1 allows the facile formation of metal hydride, which can act effectively to catalyze the hydroboration of the unsaturated C–X bond. However, the use of other solvents such as tetrahydrofuran (THF) and hexane (Hex) resulted in a drastic decrease in the formation of alkenyl boranes (Table 1, entries 7 and 8). Additionally, reduction of the amount of catalyst (0.5 mol %) for the same reaction furnished a lower yield (Table 1, entry 9). Thus, based on the above observations, to achieve...
In contrast, the hydroboration reaction of organic nitriles did not proceed smoothly at room temperature with 1 equiv of HBpin in toluene (Table S2, entry 2, SI). However, when the same reaction was carried out using 1 equiv of benzonitrile (PhCN) with 2.2 equiv of HBpin in neat condition at 1 mol % catalyst loading under an elevated temperature (60 °C), a greater yield (99%) of diborylamine (Table S2, entry 3, in SI) was achieved within 2 h of reaction time. A solvent-free approach, as well as using an earth-abundant and inexpensive metal as the catalyst for the hydroboration of organic alkynes and nitriles, not only simplifies the experimental reaction but also reduces the amount of waste which, in turn, decreases the environmental impact. Thus, considering the importance of hydroboration reactions as intermediate stages in several organic syntheses, this new atom-economic and sustainable methodology would significantly change synthetic strategies for hydroboration, compared to current expensive methods involving lanthanide, noble metals, and group 1 and 2 metals.

Table 2. Titanium-Catalyzed Hydroboration of Alkynes with HBpin

| R = alkyl, aryl | Cat 1 (1 mol %) | Toluene | R = alkyl, aryl |
|----------------|----------------|---------|----------------|
| 5a, 99%, 99b, 1 h | 5b, 97%, 98b, 2 h | 5c, 98%, 97b, 2 h | 5d, 82%, 89b, 3 h |
| 5e, 97%, 94b, 2 h | 5f, 98%, 98b, 2 h | 5g, 98%, 97b, 2 h | 5h, 95%, 82b, 3 h |
| 5i, 89%, 93b, 3 h | 5j, 96%, 94b, 1 h | 5k, 96%, 94b, 2 h | 5l, 95%, 90b, 2 h |
| 5m, 95%, 90b, 2 h | 5n, 99%, 99b, 3 h | 5o, 91%, 84b, 3 h |

“Isolated yield. "Ratio of regioisomers was determined by 1H NMR spectroscopy. The yield was calculated by 1H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture. “Reaction conditions: catalyst I (1 mol %), alkynes (1 equiv), HBpin (1.1 equiv), in toluene at rt.

Table 3. Titanium-Catalyzed Hydroboration of Nitriles with HBpin

| R = alkyl, aryl | Cat 1 (3 mol%) | Neat | R = alkyl, aryl |
|----------------|----------------|------|----------------|
| 6a, 99%, 2h | 6b, 99%, 5h | 6c, 93%, 5h | 6d, 97%, 5h |
| 6e, 97%, 7h | 6f, 99%, 5h | 6g, 98%, 7h | 6h, 82%, 8h |
| 6i, 99%, 1h | 6j, 91%, 8h | 6k, 97%, 3h | 6l, 97%, 7h |
| 6m, 97%, 3h | 6n, 97%, 7h |

“Reaction conditions: catalyst I (3 mol %), nitriles (1 equiv), HBpin (2.2 equiv), neat condition at 60 °C; the yield was calculated by 1H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture with respect to HMB (15 mol %) as the internal standard.
The titanium catalyst (complex 1) can act as an effective catalyst for the facile hydroboration of terminal alkynes and organic nitriles also, yielding \((E)\)-alkenyl boranes and diborylamines with a wide substrate scope, including broad functional group compatibility.

With these optimized conditions, we examined the scope of hydroboration reactions of various terminal alkynes \(\equiv \) bearing aryl, alkyl, and heterocyclic groups \(\equiv \) with HBpin, and the results are summarized in Table 2. Terminal alkynes with both electron-donating \((p\text{-}toly)-\text{acetylene or } 1\text{-ethynyl-4-methoxybenzene}\) and electron-withdrawing groups \((\text{fluoro, chloro, and bromo groups})\) were successfully converted to the corresponding \((E)\)-alkenyl boronates in excellent yields within a period of 2 h (Table 2, entries 5b−g). In each case, the quantum of the resulting \((E)\)-alkenyl borane product was calculated as an isolated yield. Several terminal alkynes with cyclic substituents such as cyclopentylacetylene and cyclohexylacetylene were compatible with this reaction and afforded the desired products in good yield within 3 h (Table 2, entries 5h and 5i). Terminal alkynes bearing a heteroatom, such as 3-ethynylthiophene, exhibited good tolerance and were converted to the corresponding product smoothly (Table 2, entry 5n). Additionally, aliphatic alkynes with longer alkyl chains were also effectively converted to the corresponding alkylboranes in excellent yields (Table 2, entries 5j−m). Therefore, this titanium-catalyzed hydroboration of alkynes demonstrated complete regioselectivity by the exclusive formation of the \(E\)-isomer (Figures S25−S67 in the SI). In the case of aliphatic and cyclic alkynes, the yield was calculated as NMR yield.

Next, to explore the efficiency of the titanium catalyst 1, we investigated the hydroboration reactions of various nitriles with HBpin, and representative results are summarized in Table 3. Aryl nitriles with both electron-donating groups, such as \(-\text{Me, } -\text{OMe, } -\text{SMe, and } t\text{-Bu groups}\) and electron-withdrawing groups, such as \(-\text{F, } -\text{Cl, } -\text{Br, and } -\text{CF}_3\) groups, afforded the desired diborylamine products in excellent yield (95−99%) within 3 or 4 h at 60 °C (Table 3, entries 6b−i). Where alkyl nitriles were used as the substrates, the hydroboration reaction proceeded at a higher rate and resulted in the formation of \([R\text{CH}_2\text{N(Bpin)}_2]\) in quantitative yields (95−99%) within 1−3 h of reaction time (Table 3, entries 6l−n). To our delight, extension of the protocol to nitriles bearing a heteroatom, such as 2-(thiophene-2-yr)acetonitrile, demonstrated very good tolerance for thiophene moieties (99%, Table 3, entry 6o). Additionally, dinitriles could also be converted to the desired diboryl product smoothly, with up to 91% yield in 10 h (Table 3, entry 6p). In all cases, yields of the products were calculated from 1H NMR analysis using hexamethylbenzene (HMB) as an internal standard (Figure S68−S118 in the SI).

Further, to check the chemoselectivity of complex 1 for the hydroboration of alkynes and nitriles, we treated 4-acetoxy phenylacetylene and 4-acetoxy benzonitrile with HBpin—keeping the ester moiety unperturbed in both cases—to exclusively obtain the resulting products of hydroboration of the alkylene as well as nitrile functionalities within 3−6 h of reaction time (Table 4, entries 5q and 6q; Figures S156−S160).
in the SI). Additionally, when a 1:1 mixture of 4-bromo-phenylacetylene and 4-methyl styrene was used as the substrate in this reaction, the hydroboration of the alkyne moiety proceeded selectively to give product 5g with a near-quantitative recovery of styrene (Table 4, entry 1). Similar chemoselectivity was observed when a mixture of 1-ethynyl-4-methylbenzene and 4-bromo-styrene or ethynylcyclohexane and 4-methoxy-styrene was used under analogous reaction conditions (Table 4, entries 2 and 3; Figures S148−S153 in the SI). A similar result was also obtained when 1-ethynylcyclohex-1-ene was used as the substrate in which the catalyst selectively reduced the triple bond, while keeping the internal double bond unperturbed (Table 4, entry 5p; Figures S154−S155 in the SI).

Further, we wanted to isolate the end products of the catalytic hydroboration of alkynes and nitriles. The alkenyl boranes underwent rapid protonolysis with acetic acid at room temperature to form the corresponding terminal olefins of high purity from terminal acetylenes (Table 5, entries 7a−f; Figures S119−S130 in the SI). However, the diborylamines yielded a moderate quantity of the corresponding substituted benzyl ammonium chloride upon protonolysis in aqueous HCl (0.05 M) at room temperature (Table 6, entries 8a−c; Figures S131−S136 in the SI).

Subjecting 1-deuterium-2-phenylacetylene and its methyl and bromo derivatives (9a−c) to HBpin resulted in the exclusive formation of the (Z)-vinyl boronate, containing deuterium at the terminal carbon (Scheme 2). The proton resonance signals, at a chemical shift of 6.07−6.1 ppm for complex 10a, 6.03−5.99 ppm for complex 10b, and 6.17−6.13 ppm for complex 10c, were absent in the 1H NMR spectra. The additional singlet peak generated at 7.01 ppm confirmed the position of deuterium at the phenyl-substituted terminal carbon (PhCH═CD) (Figures S137−S147 in the SI).

Three separate control reactions were carried out using 4-methylphenylacetylene and 4-trifluorobenzonitrile with HBpin in the presence of only ligand L1 in set 1 and using Ti(NMe2)4 in sets 2 and 3. From the NMR spectra (Figures S161−S164 in the SI), it was observed that in the presence of only ligand L1-H2, even when higher loading (30 mol %) was used, no traces of product were formed. However, hydroboration in the presence of only Ti(NMe2)4 (10 mol %) yielded 48% conversion of nitrile to diborylamine and 40% conversion of alkyne to alkenyl boranes in 15 h. The pyrophoric nature of the Ti(NMe2)4 is considered a major disadvantage for its use as a catalyst (Figures S165−S171 in the SI). A control reaction was also carried out for the hydroboration of thiophenecarbonitrile with HBpin in the presence of only Ti(NMe2)4 (10 mol %) in toluene, which also showed no traces of a product being formed (Figures S172−S173 in the SI).

Table 5. Hydrolysis of (E)-Alkenyl Boranes To Give Alkenes

| R             | Cat (1 mol %) | Glacial Acetic acid | R'                 |
|---------------|---------------|---------------------|--------------------|
| ary1          | Toluene, rt, 1 - 3 h | toluene | H₂O | (7a-7f) |

| 7a, 85%       | 7b, 84%       | 7c, 78%       | 7d, 80%       | 7e, 74%       | 7f, 72%       |

*Isolated yields are shown; reaction conditions: catalyst 1 (1 mol %), alkynes (1 equiv), HBpin (1.1 equiv), in toluene at rt. To the reaction mixture was added 5.0 mL of glacial acetic acid, and the mixture allowed to stand overnight (12 h).

Table 6. Hydrolysis of Diborylamines To Give Primary Amines

| R-CN | Cat (1 mol %) | HCl | NH₃Cl |
|------|---------------|-----|-------|
| ary1 | Neat, 60 °C, 2 - 10 h |      |    |

| 8a, 80%       | 8b, 81%       | 8c, 75%       |

*Isolated yields are shown; chemical yields of diborylamines in divagation. Reaction conditions: catalyst 1 (3 mol %), nitriles (1 equiv), HBpin (2.2 equiv), neat condition at 60 °C.

Scheme 2. Reaction with Deuterium-Labeled Terminal Alkynes

[Scheme diagram]

“The yield was calculated by 1H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture.
Initially, the titanium precatalyst 1 reacts with HBpin to form the active titanium hydride species (I). Attempts to isolate the intermediates generated and their characterization through crystallization were unsuccessful. However, this step is well known in the literature.49,50 The titanium hydride species further reacts with the alkynes and nitriles and affords the corresponding metal alkynyl species (III) and metal imine species (A and B in the SI) via sigma bond metathesis. In the case of hydroboration of alkynes, the titanium alkynyl species is regenerated and takes part in the catalytic cycle. However, in the case of hydroboration of nitriles, the metal imine complex (B) reacts with another molecule of HBpin to yield alkenyl borane dimethyl sulfide (D). In the next step, the active titanium hydride species (I) reacts with another molecule of HBpin to yield alkenyl (III) reacts with another molecule of HBpin to form a four-membered species (C), which eventually rearranges itself to yield boryl amine (D). In the next step, the boryl amine D reacts with another HBpin molecule to afford the diborylamine titanium species (E). In the final step, the active titanium hydride species is regenerated by emitting the corresponding free diborylamine product.

**CONCLUSIONS**

In summary, in this paper, we have demonstrated the synthesis, structure, and catalytic application of titanium and zirconium complexes of the amidophosphine–borane ligand. Ti^IV^ complex [([Ph2P(BH3)N]2C6H4)2Ti(NMe2)2] (1), mixed bicyclopentadienyl amidophosphine–borane zirconium complex [η5-(C5H5)2Zr[Ph2P(BH3)N]2C6H4] (2), zirconium dichloride complex [([Ph2P(BH3)N]2C6H4)2ZrCl2] (3), and homoleptic zirconium complex [([Ph2P(BH3)N]2C6H4)Zr] (4) were prepared in excellent yields, and the solid-state molecular structures of complexes 1, 2, and 4 were established. Among these complexes, the Ti^IV^ complex 1 was found to be a competent catalyst for the alkyne hydroboration of a large number of alkynes with different functional groups and afforded the corresponding (E)-alkenyl boronate esters with a high degree of chemoselectivity at ambient temperature. Additionally, complex 1 effectively catalyzed the chemo-selective hydroboration of organic nitriles to yield N,N-diborylamines with a broad substrate scope, having both aliphatic and aromatic nitriles, in short reaction times.

**EXPERIMENTAL SECTION**

**General Experimental Procedures.** All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or an argon-filled glovebox. CDCl3 was distilled and stored in the glovebox. 1H NMR (400 MHz), 13C{1H} NMR (100 MHz), 31P{1H} NMR (161.9 MHz), 11B{1H} (128.3 MHz), and 19F (376 MHz) spectra were measured on a Bruker AVANCE III-400 spectrometer. Elemental analyses were performed on a Bruker EURO EA at the Indian Institute of Technology Hyderabad. All of the starting materials, including o-phenylenediamine, chlorodiphenylphosphine, tetrakisdimethylamido titanium(IV), zirconocene dichloride [(C5H5)2ZrCl2], zirconium tetrachloride, and alkynes, as well as organic nitriles were purchased from Sigma-Aldrich, India, and used without further purification, and boranes were purchased from Sigma-Aldrich, India, and distilled before being used. The starting materials, 2-ethyl anisole, methyl 4-ethylbenzoxazole, phenylacetylene-0, 4-methylphenylacetylene-0, and 4-bromophenylacetylene-0, were synthesized according to procedures published in the literature.

**Preparation of Ligand** [([Ph2P(BH3)NH]2C6H4) (L1-H2)]. To a solution of o-phenylenediamine (616 mg, 5.7 mmol) and triethylamine (1.09 g, 1.56 mL, 11.4 mmol) being stirred in a THF/CH2Cl2 mixture, a solution of chlorodiphenylphosphine (2 mL, 11.4 mmol) in THF (5 mL) was added dropwise, and the reaction mixture was stirred for another 3 h. The precipitate was filtered, and the solvent was removed in vacuo. To this residue, 20 mL of dry toluene and 2 equiv of borane dimethyl sulfide (1.2 mL, 11.4 mmol) were added and stirred for a further 12 h. The title compound was formed as a white precipitate. It was purified by washing several times with n-hexane. Crystals suitable for X-ray diffraction analysis were obtained from THF/n-pentane combination in a 1:2 ratio. The title compound [([Ph2P(BH3)NH]2C6H4) (1-H2)] is soluble in CDCl3, CH2Cl2, THF, and toluene. The compound 1-H2 was recrystallized from hot toluene. Yield (1.53 g, 2.9 mmol) (58.7%). 1H NMR (400 MHz, C6D6): δH = 7.62–7.57 (m, 8H, ArH), 7.39–7.37 (m, 12H, ArH), 7.36–7.18 (m, 2H, ArH), 6.70–6.68 (m, 2H, ArH), 4.52 (d, 2H, J = 4 Hz, NH), 1.19 (br, 6H, BH3) ppm. 13C{1H} NMR (100 MHz, C6D6): δC = 132.4 (ArC), 132.1 (ArC), 131.9 (P attached ArC), 131.6 (P attached ArC), 130.7 (P attached o-Arc), 130.1 (P attached o-Arc), 128.9 (P attached p-Arc), 128.8 (P attached m-Arc), 124.1 (m-Arc), 123.4 (o-Arc) ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 56.0 (d, J = 85.8 Hz) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = −38.1 (br) ppm. Fourier transform infrared (FT-IR) (selected frequencies): ν = 3338 (N–H), 1434 (P–C), 999 (P–N), 2383 (B–H), 602 (P–B) cm⁻¹. Elemental analysis: [([Ph2P(BH3)NH]2C6H4)] (504.14): calc (%) C 71.47, H 6.40, N 5.56; found C 71.30, H 6.21, N 5.22.

**Preparation of Complex** [([Ph2P(BH3)NH]2C6H4)Zr(NMe2)] (1). In a 50 mL dry Schlenk flask, ligand L1-H2 (129 mg, 0.256 mmol) and Ti(NMe2)4 (40 mg, 0.256 mmol) were mixed together in 10 mL of toluene at an ambient temperature and...
stirred for 6 h. The resultant filtrate was dried in vacuo. The resulting red compound was further purified by washing with n-pentane, and crystals suitable for X-ray analysis were grown from toluene at −35 °C. Yield (171 mg, 0.268 mmol) (78%). 1H NMR (400 MHz, CD2Cl2): δH 7.87−7.83 (m, 8H, ArH), 7.03−6.90 (m, 14H, ArH), 6.53−6.52 (m, 2H, ArH), 3.21 (s, 12H, NMMe2), 2.11 (s, 6H, BHH3) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 127.9 (P-ArC), 127.7 (P-ArC), 45.1 ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 74.1 ppm. 13C{1H} NMR (100 MHz, C6D6): δC = 137.6 (P-ArC), 135.9 (P-ArC), 123.2 (o-ArC), 132.1 (m-ArC), 128.2 (P-ArC), 128.1 (p-ArC), 127.9 (ArC), 127.7 (ArC) ppm. 1H NMR (400 MHz, C6D6): δH = 7.58−7.57 (m, 6H, ArH), 7.19−6.18 (m, 4H, ArH), 6.99−6.90 (m, 14H, ArH), 6.00 (s, 10H, Cp-H), 1.93 (br, 6H, BHH3) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 137.9 (P-ArC), 129.3 (P-ArC), 128.8 (o-ArC), 128.6 (m-ArC), 128.3 (p-ArC), 127.8 (P-ArC), 125.7 (ArC), 116.4 (ArC) ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 69.8 ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = −35.2 (br) ppm. Elemental analysis: [C40H40B2N2P2Zr] (722.2): calcd (%) C 65.78, H 5.52, N 7.71, P 7.41, B = 24.2, Zr = 4.03. Yield (134.4 mg, 0.256 mmol) (92%). 1H NMR (400 MHz, CD2Cl2): δH = 7.30−7.27 (m, 1H, ArH), 7.25−7.19 (m, 5H, ArH), 7.18−7.14 (m, 6H, ArH), 7.06−6.99 (m, 14H, ArH), 6.99−6.90 (m, 14H, ArH), 6.00 (s, 10H, Cp-H), 1.93 (br, 6H, BHH3) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 137.9 (P-ArC), 129.3 (P-ArC), 128.8 (o-ArC), 128.6 (m-ArC), 128.3 (p-ArC), 127.8 (P-ArC), 125.7 (ArC), 116.4 (ArC) ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 69.8 ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = −34.9 (br) ppm. Elemental analysis: [C40H40B2N2P2Zr] (722.2): calcd (%) C 66.40, H 5.57, N 3.87; found C 66.14, H 5.71, N 3.82.

Preparation of Complex [η5-(C5H5)Zr(Ph2P(BH3)N)2C6H4J2] (2). In a 50 mL dry Schlenk flask, a suspension of ZrCl3.5H2O (74 mg, 0.256 mmol) in 3 mL of toluene was added dropwise to a freshly prepared 5 mL toluene solution containing a mixture of ligand L1-H2 (129 mg, 0.256 mmol) and LiN(SiMe3)2 (85 mg, 0.512 mmol) at an ambient temperature and stirred for 6 h. The white precipitate of LiCl was filtered through a G4-frit and dried in vacuo. The resulting red compound was purified by washing with n-pentane, and crystals suitable for X-ray analysis were grown from toluene at −35 °C. Yield (149.9 mg, 0.199 mmol) (81%). 1H NMR (400 MHz, CD2Cl2): δH 7.58−7.57 (m, 6H, ArH), 7.19−6.18 (m, 4H, ArH), 6.99−6.90 (m, 14H, ArH), 6.00 (s, 10H, Cp-H), 1.93 (br, 6H, BHH3) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 137.9 (P-ArC), 129.3 (P-ArC), 128.8 (o-ArC), 128.6 (m-ArC), 128.3 (p-ArC), 127.8 (P-ArC), 125.7 (ArC), 116.4 (ArC) ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 69.8 ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = −35.2 (br) ppm. Elemental analysis: [C50H50B2N2P2Ti] (722.2): calcd (%) C 65.78, H 5.52, N 7.71, P 7.41, B = 24.2, Zr = 4.03. Yield (134.4 mg, 0.256 mmol) (92%). 1H NMR (400 MHz, CD2Cl2): δH = 7.30−7.27 (m, 1H, ArH), 7.25−7.19 (m, 5H, ArH), 7.18−7.14 (m, 6H, ArH), 7.06−6.99 (m, 14H, ArH), 6.99−6.90 (m, 14H, ArH), 6.00 (s, 10H, Cp-H), 1.93 (br, 6H, BHH3) ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 137.9 (P-ArC), 129.3 (P-ArC), 128.8 (o-ArC), 128.6 (m-ArC), 128.3 (p-ArC), 127.8 (P-ArC), 125.7 (ArC), 116.4 (ArC) ppm. 31P{1H} NMR (161.9 MHz, C6D6): δP = 69.3 ppm. 11B{1H} NMR (128.4 MHz, C6D6): δB = 24.2, −36.5 ppm. However, a satisfactory elemental analysis could not be performed due to high oxygen and moisture sensitivity of the complex.

General Procedure for Hydroboration of Terminal Alkynes 5a−q. Catalyst 1 (1 mol %) was placed in a Schlenk tube, to which alkynes (1.0 mmol) as well as HBpin (1.1 mmol) were added inside a glovebox. After this, toluene (0.25 mL, in the case of the solid substrate) was added to the reaction mixture and the Schlenk tube was allowed to be stirred at room temperature for 1 h under an inert atmosphere. The products were isolated by washing with a mixture of ethyl acetate and hexane (02:98) as eluent.

General Procedure for the Synthesis of Compounds 6a−q. Catalyst 1 (3 mol %), nitriles (1 mmol), and HBpin (2.2 mmol) were added in a 25 mL Schlenk flask equipped with a magnetic stir bar inside a glovebox. The reaction mixture was stirred at 60 °C for 1−8 h depending on the nature of the starting materials. The progress of the reaction was monitored by 1H NMR spectroscopy using hexamethyldisiloxane (15 mol %) as an internal standard. After the reaction was completed, excess HBpin was evaporated under reduced pressure to obtain the desired compounds.

X-ray Crystallographic Analyses. Single crystals of complexes 1, 2, and 4 were grown from a concentrated solution of toluene at −35 °C. A crystal of suitable dimensions of complexes 1, 2, and 4 were mounted on a Cryoloop (Hampton Research Corp.) with a layer of light mineral oil. Crystals of complexes 1, 2, and 4 were measured at 150 K. All measurements were recorded on a Rigaku SuperNova X−calibur Eos CCD detector with graphite monochromatic Cu Kα (1.54184 Å) radiation. Crystal data and structure refinement parameters of complexes 1, 2, and 4 are summarized in Table S1. The structures were solved by direct methods (SIR2004)50 and refined on F2 by full-matrix least−
squares methods, using SHELXL-2016/6.\textsuperscript{31} Nonhydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $\sum w(Fo^2 - Fe^2)^2$ (where $w = 1/(\sigma^2(Fo) + (4Fo^2/3))$, where $P = (\text{Max}(Fo^2,0) + 2Fe^2)/3$ with $\sigma^2(Fo)$ from counting statistics. The functions $R_1$ and $wR_2$ were $\sum ||Fo - Fe||/\sumFo$ and $\sum w(Fo^2 - Fe^2)^2/\sum(wFo^2)^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of complexes 1, 2, and 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1903181 (complex 1), 1917671 (complex 2), and 1917672 (complex 4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: + (44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

\section*{Associated Content}

\section*{Supporting Information}
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03598.

$^1$H and $^{13}$C($^1$H), NMR spectra, mass spectra, and combustion analyses of all (E)-alkenyl boranes, diborurate amines, substituted alkyl and aryl alkenes, and substituted benzyl ammonium chloride, as well as deuterium derivatives of alkenyl boranes, complexes 5a–q, 6a–q, 7a–f, 8a–c, 9a–c, and 10a–c (PDF)

Crystallographic data of 2 (CIF)

Crystallographic data of 1 (CIF)

Crystallographic data of 4 (CIF)

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Notes
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