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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 Ti^{IV} complex $[\{Ph_2P(BH_3)N\}_2C_6H_4Ti(NMe_2)_2]$ (**1**) was obtained by the reaction between tetrakis-(dimethylamido)titanium(IV) and the protic aminophosphine−borane ligand $[\{Ph_2P(BH_3)NH\}_2C_6H_4]$ (**LH2**) at ambient temperature. Both the heteroleptic zirconium complexes—$[\eta^5\text{-}(C_5H_5)_2Zr\{Ph_2P\text{-}(BH_3)N\}_2C_6H_4]$ (**2**) and $[[\{Ph_2P(BH_3)N\}_2C_6H_4]ZrCl_2]$ (**3**)—and the homoleptic zirconium complex $[[\{Ph_2P(BH_3)\text{-}N\}_2C_6H_4]_2Zr]$ (**4**) were obtained in good yield by the salt metathesis reaction of either zirconocene dichloride $[\eta^5\text{-}(C_5H_5)_2ZrCl_2]$ or zirconium tetrachloride with the dilithium salt of the ligand $[\{Ph_2P(BH_3)NLi\}_2C_6H_4]$ (**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[1] and natural product syntheses,[2] as well as the foundation for several chemical transformations in the pharmaceutical industry.[3] Vinyl boronates are effectively used as synthons in organic chemistry,[4] in aldol reactions,[5] in diverse coupling reactions; they are also used as Michael donors.[6] 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.[7−10] 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.[11] 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,[12] Co,[13] Cu,[14] Ru,[15] Rh, and Ir.[16] Additionally, there are some reports of hydroboration of carbonyl compounds affording boronic esters, catalyzed by Co, Fe, and Ru.[17−23] Main-group metal-catalyzed hydroboration of terminal alkynes and organic nitriles is also well reported in the literature.[24−29] Using commercially available aluminum hydride ($^{i}Bu_2AlH$) and $LiAlH_4$ or sodium borohydride ($NaBH_4$) is a well-known means of reduction of alkynes and alkenes, followed by aryl and alkyl nitriles.[29] 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

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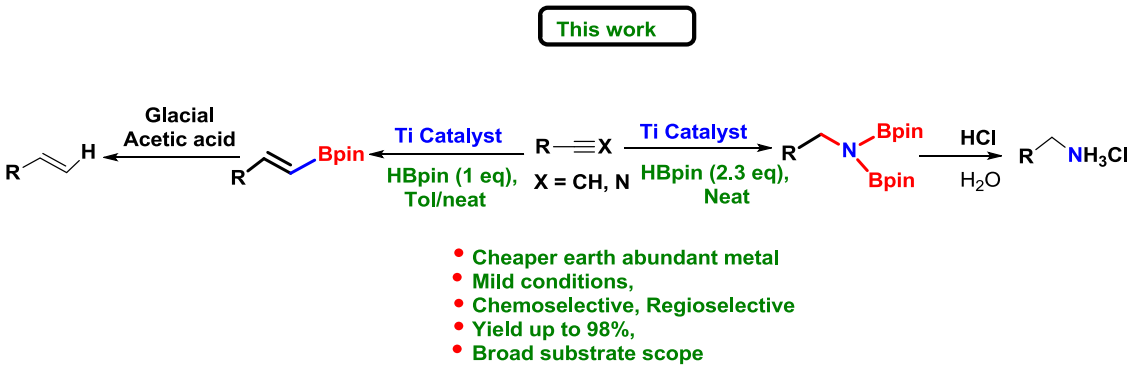
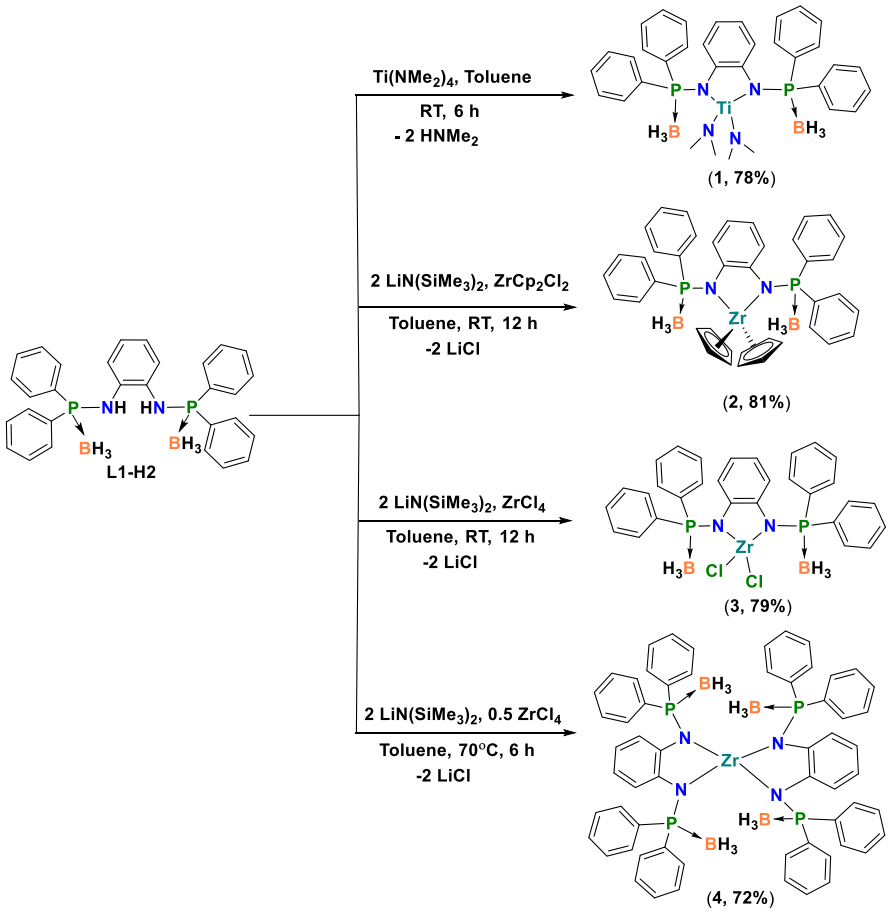


Figure 1. Catalytic reduction of alkynes and nitriles to alkenes and primary amines, respectively.

Scheme 1. Synthesis of Titanium (Complex 1) and Zirconium Complexes (Complexes 2−4) from L1-H2



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

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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 aminophosphine−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 aminophosphine ligand (**L1-H2**), which was synthesized by the reaction between *N*,*N*′-bis-(diphenylphosphino)-benzene-1,2-diamine [$Ph_2PNHC_6H_4NH$-PPh_2] and dimethyl sulfide borane complex in a 1:2 molar ratio in toluene (Tol) at room temperature (rt).[42,43] The titanium complex, with the molecular formula [$\{Ph_2P(BH_3)N\}_2C_6H_4Ti(NMe_2)_2$] (**1**) was synthesized utilizing 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 (Cp_2ZrCl_2) with dianionic lithium salt [$\{Ph_2P(BH_3)$-$N\}_2C_6H_4]Li_2(THF)_4$ afforded the corresponding bis-cyclopentadienyl zirconium complex [$Cp_2Zr\{Ph_2P(BH_3)N\}_2C_6H_4$] (**2**) in good yield with the elimination of 2 equiv of lithium chloride (Scheme 1). The heteroleptic zirconium dichloride complex [[$\{Ph_2P(BH_3)N\}_2C_6H_4$]$ZrCl_2$] (**3**) and homoleptic zirconium complex [[$\{Ph_2P(BH_3)N\}_2C_6H_4]_2Zr$] (**4**) were isolated in good yield through the one-pot treatment of ligand **L1-H2** and lithium bis(trimethylsilyl)amide [$LiN(SiMe_3)_2$] with $ZrCl_4$ in a 1:2:1 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 affirmed 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 δ_H 4.84 ppm, assigned to −NH protons for the free ligand, confirmed the formation of fragments of the dianionic ligand **L1** [Figures S5, S9, S13, and S17 in the Supporting Information (SI)]. Additionally, the characteristic singlet resonance at δ_H 3.21 ppm confirmed the presence of two dimethylamido groups [$-N(CH_3)_2$] in complex **1** and resonances of the cyclopentadienyl protons in complex **3** appeared at δ_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 $^{31}P\{^1H\}$ NMR spectral data, the complexes exhibited sharp signals at δ_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** (δ_P 56.8 ppm) (Figures S7, S11, S15, and S19 in the SI). In the $^{11}B\{^1H\}$ NMR spectra, a broad doublet signal centered at δ_B −34.9 (complex **1**), −35.2 (complex **2**), −34.9 (complex **3**), and −35.1 (complex **4**) ppm was observed, which was in the range (−35.4 ppm) similar to that of the starting material **L1-H2** (Figures S6, S10, S14, and S18 in the SI).

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 °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 $P2_1/c$, with four molecules in the unit cell. The coordination polyhedron is formed by the chelation of ligand **L1**, which is bonded to the Ti^{IV} metal ion through two amido nitrogen atoms. Additionally, two dimethylamido groups are attached to the Ti^{IV} ion to adopt a distorted tetrahedral geometry. A distance of 2.284 Å (Ti−H2a) was observed between the B−H hydrogen atom and the Ti^{IV} metal ion of complex **1**, presumably due to crystal packing (Figure 2). However, in the ^1H NMR spectra, all of the BH_3 protons exhibited at δ_H 2.11 ppm, indicating that both the borane groups are chemically equivalent in complex **1**.

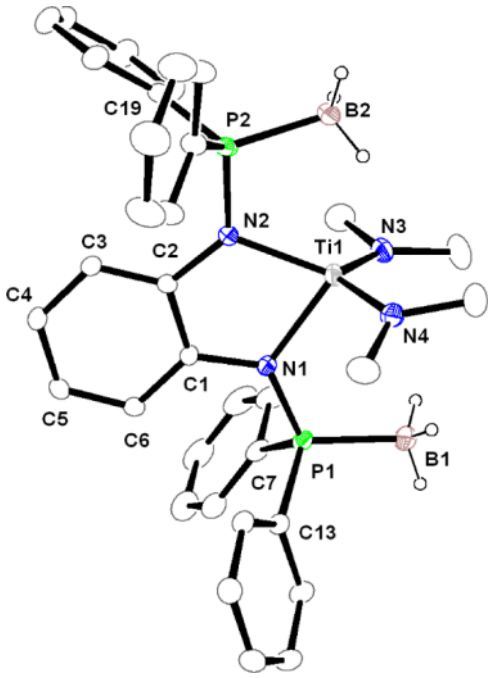

Figure 2. Solid-state structure of complex **1**. Hydrogen atoms are omitted for clarity (except BH_3). Selected bond lengths (Å) and bond angles (deg): Ti1−N4 1.871(2), Ti1−N3 1.874(2), Ti1−N2 2.0286(18), Ti1−N1 2.0809(17), P1−N1 1.6757(17), P1−C13 1.823(2), P1−C7 1.827(2), P1−B1 1.908(3), P2−N2 1.6513(18), P2−C19 1.810(2), P2−C25 1.813(2), P2−B2 1.912(3), N4−Ti1−N3 118.15(9), N4−Ti1−N2 119.32(8), N3−Ti1−N2 120.48(8), N4−Ti1−N1 100.50(8), N3−Ti1−N1 106.57(8), N2−Ti1−N1 76.98(7), N1−P1−B1 115.23(11), N2−P2−B2 102.91(11).

Zirconium complex **2** crystallizes in the triclinic space group $P\bar{1}$, 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 dianionic ligand **L1**, along with η5-coordination of two cyclopentadienyl moieties to the Zr^{IV} ion, adopting an 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

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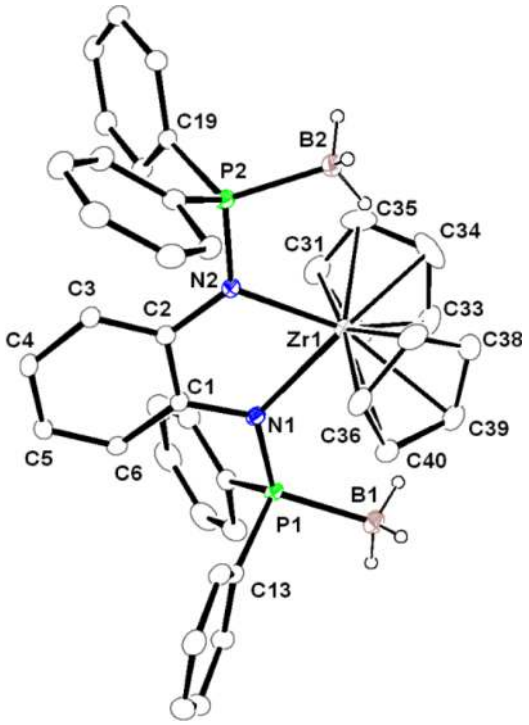


Figure 3. Solid-state structure of compound **2**. Hydrogen atoms are omitted for clarity (except BH_3). Selected bond lengths (Å) and bond angles (deg): Zr1−N1 2.2877(19), Zr1−N2 2.2073(19), Zr1−C39 2.527(3), Zr1−C33 2.536(3), P1−N1 1.6738(19), P1−C13 1.835(2), P1−C7 1.838(3), P1−B1 1.949(3), P2−N2 1.6565(19), P2−C19 1.818(3), P2−C25 1.821(3), P2−B2 1.919(3), N2−Zr1−N1 73.01(7), N2−Zr1−C34 123.87(12), N1−P1−B2 122.08(12), N2−P2−B2 104.40(11), Zr1−C32−H32 117.7.

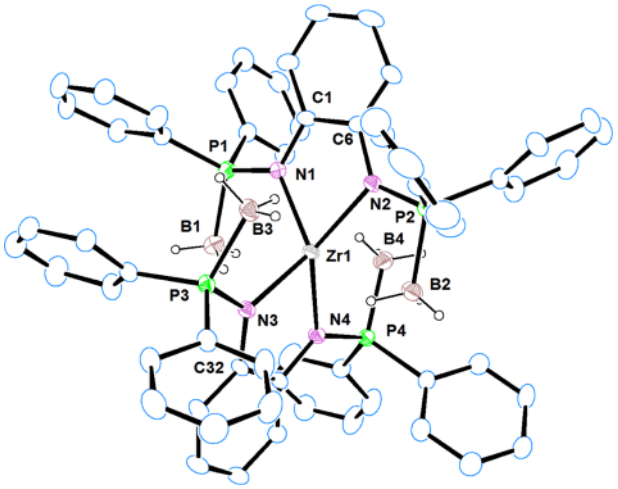


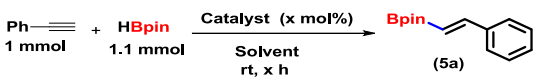
Figure 4. Solid-state structure of compound **4**. Hydrogen atoms are omitted for clarity (except BH_3). Selected bond lengths (Å) and bond angles (deg): Zr1−N1 2.2185(5), Zr1−N2 2.208(5), Zr1−N3 2.168(5), Zr1−N4 2.203(5), P1−B1 1.881(9), B3−P3 1.915(8), P1−C7 1.814(7), P2−B2 1.900(8), P1−N1 1.643(5), P2−N2 1.643(5), P3−N3 1.662(5), N1−C1 1434(8), N1−Zr1−N2 74.0(2), N3−Zr1−N2 134.27(19), N3−Zr1−N1 115.93(19), N4−Zr1−N3 73.10(18), N4−Zr1−N2 136.98(18), N1−Zr1−N4 130.14(19). N1−P1−B1 106.2(3), N2−P2−B2 97.5(3), N3−P3−B3 102.5(3), N4−P4−B4 102.7(3).

2.207(19) Å] in complex **2** are slightly longer than the Ti−N distances in complex **1**; however, they are in full agreement with the Zr−N covalent bond distances reported in the literature.[44b] 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.[44]

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 Zr^{IV} metal ion, presumably due to crystal packing (Figure 2). However, in the ^{1}H NMR spectra, all of the BH_3 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).

Table 1. Optimization Table for Hydroboration of Alkynes and Nitriles Using Complex 1 as Precatalyst[a]



entry	catalyst	cat. (mol %)	solvent	T (°C)	t (h)	yield of **5a**
1			neat	60	24	0
2	1	1	neat	rt	2	92
3	1	1	Tol	rt	1	99
4	2	1	Tol	rt	1	10
5	3	1	Tol	rt	1	25
6	4	1	Tol	rt	1	0
7	1	1	THF	rt	10	30
8	1	1	Hex	rt	10	50
9	1	0.5	Tol	rt	5	72

[a]The yield was calculated using ^{1}H NMR (400 MHz) integration of a characteristic product signal present in the reaction mixture using hexamethylbenzene (HMB) (10 mol %) as an internal standard.

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

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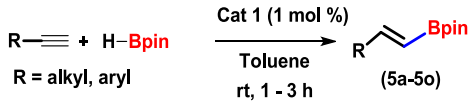
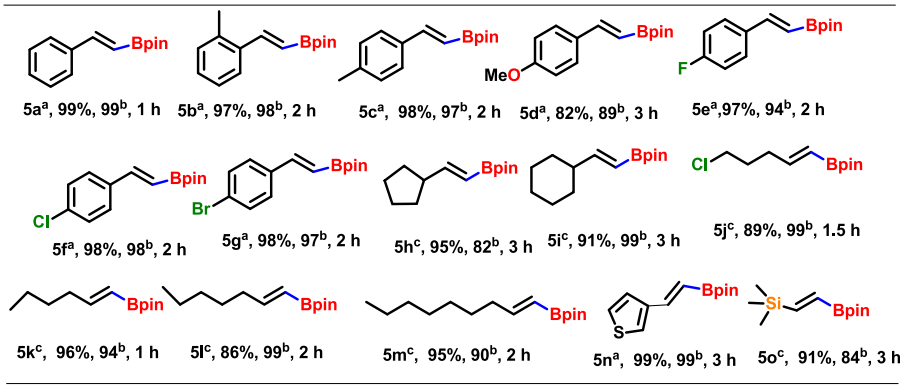
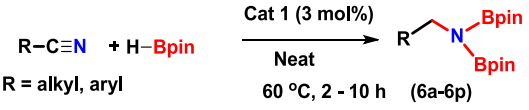
Table 2. Titanium-Catalyzed Hydroboration of Alkynes with HBpin[d]

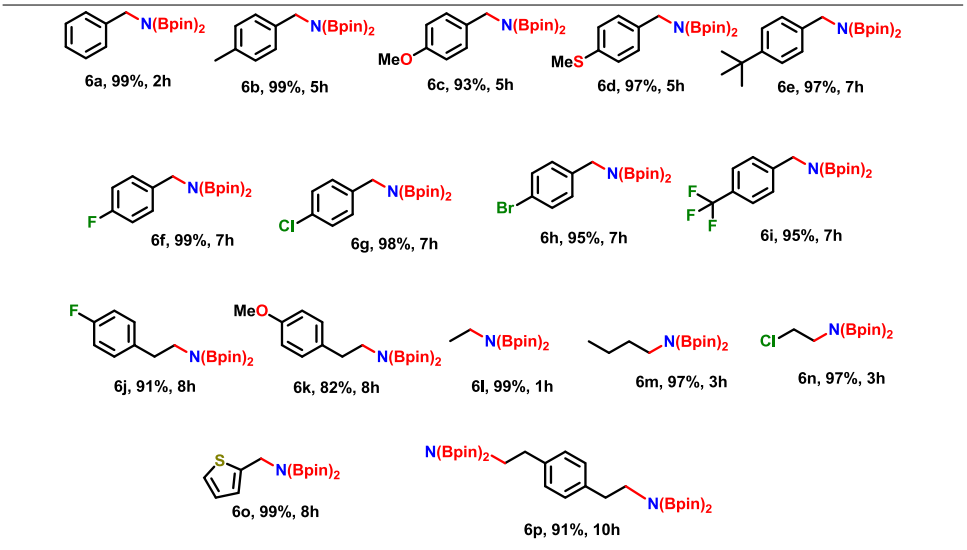




[a]Isolated yield. [b]Ratio of regioisomers was determined by ^{1}H NMR spectroscopy. [c]The yield was calculated by ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture. [d]Reaction conditions: catalyst **1** (1 mol %), alkynes (1 equiv), HBpin (1.1 equiv), in toluene at rt.

Table 3. Titanium-Catalyzed Hydroboration of Nitriles with HBpin[a]





[a]Reaction conditions: catalyst **1** (3 mol %), nitriles (1 equiv), HBpin (2.2 equiv), neat condition at 60 °C; the yield was calculated by ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture with respect to HMB (15 mol %) as the internal standard.

maximum efficiency within a short period, we decided to use 1.1 equiv of HBpin for the hydroboration reaction of alkynes by loading 1 mol % of catalyst **1** using toluene as the solvent at room temperature.

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

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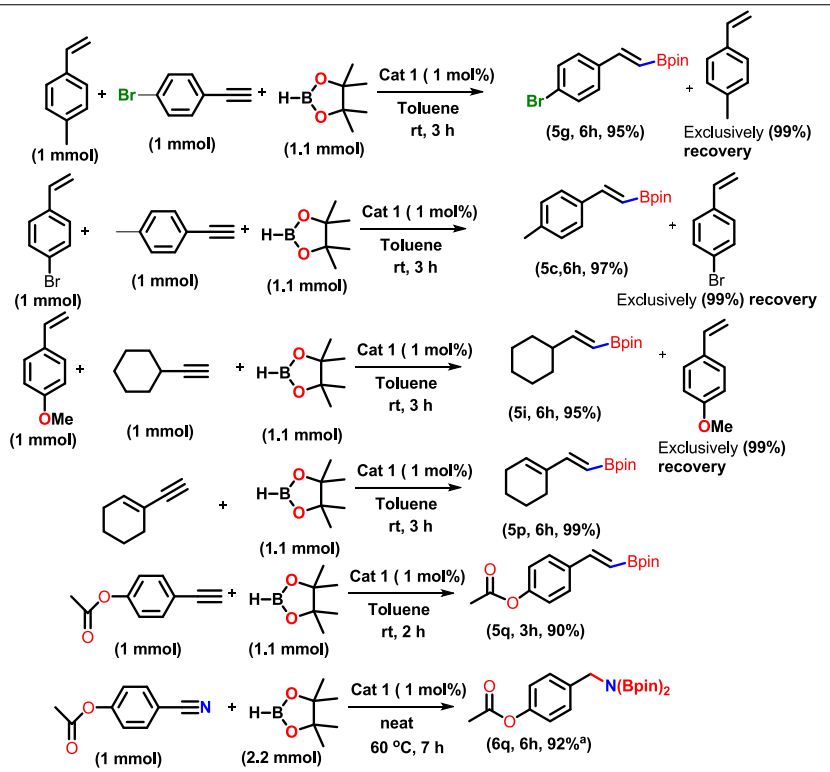
Table 4. Chemoselective Hydroboration of Alkynes and Nitriles[b]



[a]Yield was calculated by ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture with respect to HMB (15 mol %) as the internal standard. [b]Reaction conditions: catalyst **1** (1 mol %), alkynes (1 equiv), HBpin (1.1 equiv), in toluene at rt, nitriles (1 equiv), HBpin (2.2 equiv), neat condition at 60 °C; yield was calculated by ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture.

metals.[24,45,46] 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—bearing aryl, alkyl, and heterocyclic groups—with HBpin, and the results are summarized in Table 2. Terminal alkynes with both electron-donating (*p*-tolyl-acetylene or 1-ethynyl-4-methoxy-benzene) and electron-withdrawing groups (bearing 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 cyclo-hexyl-acetylene 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 alkenyl boranes in excellent yields (Table 2, entries **5j**−**m**). Therefore, this titanium-catalyzed hydro-boration 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 −Me, −OMe, −SMe, and *t*Bu groups, and electron-withdrawing groups, such as −F, −Cl, −Br, and $-CF_3$ 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 $[RCH_2N(Bpin)_2]$ 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 ^{1}H 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 alkyne as well as nitrile functionalities within 3−6 h of reaction time (Table 4, entries **5q** and **6q**; Figures S156−S160

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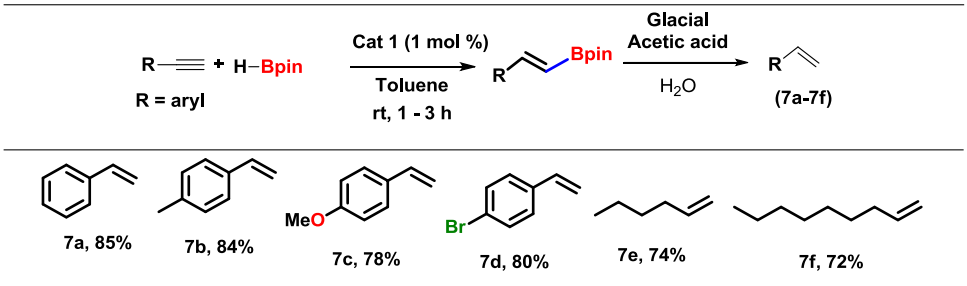
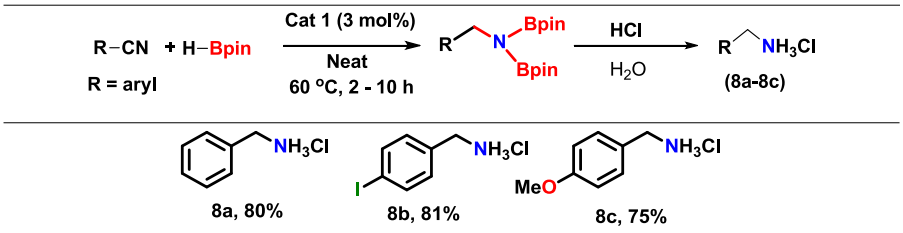
Table 5. Hydrolysis of (*E*)-Alkenyl Boranes To Give Alkenes[a]



[a]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[a]



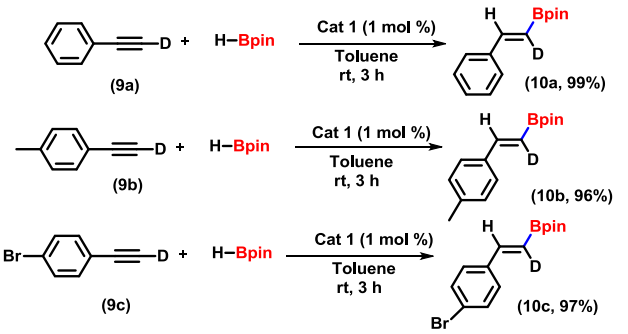
[a]Isolated yields are shown; chemical yields of diborylamines in divagation. Reaction conditions: catalyst **1** (3 mol %), nitriles (1 equiv), HBpin (2.2 equiv), neat condition at 60 °C.

in the SI). Additionally, when a 1:1 mixture of 4-bromophenylacetylene 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 ^{1}H 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).

Scheme 2. Reaction with Deuterium-Labeled Terminal Alkynes[a]



[a]The yield was calculated by ^{1}H NMR (400 MHz) integration of characteristic product signal present in the reaction mixture.

Three separate control reactions were carried out using 4-methylphenylacetylene and 4-triflurobenzonitrile with HBpin in the presence of only ligand **L1** in set 1 and using $Ti(NMe_2)_4$ 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 $Ti(NMe_2)_4$ (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 $Ti(NMe_2)_4$ 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 $Ti(NMe_2)_4$ (10 mol %) in toluene, which also showed no traces of a product being formed (Figures S172–S173 in the SI).

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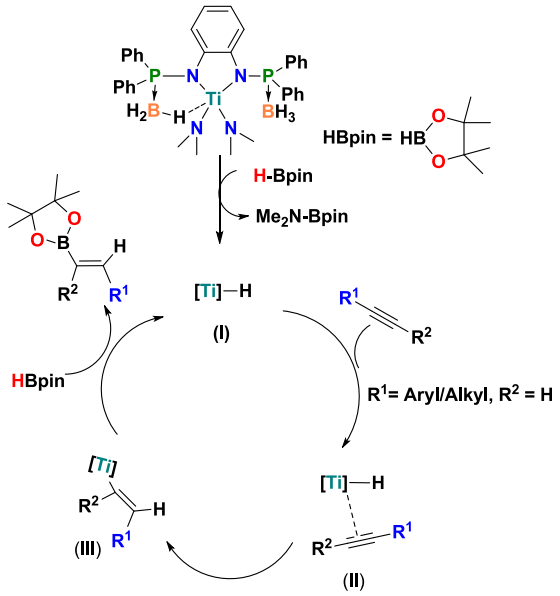
Based on previous reports in the literature and experimental results,[47,48] the most plausible mechanism for the catalytic hydroboration of alkynes and nitriles with HBpin is shown in Schemes 3 and S1 (Supporting Information), respectively.

Scheme 3. Most Plausible Mechanism for Catalytic Hydroboration Reaction of Alkynes with HBpin



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 alkenyl 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 alkene species (III) reacts with another molecule of HBpin to yield alkenyl boronate esters. In the next step, the active titanium hydride 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 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 $[\{Ph_2P(BH_3)\text{-}N\}_2C_6H_4Ti(NMe_2)_2]$ (**1**), mixed bis-cyclopentadienyl amidophosphine−borane zirconium complex $[\eta^5\text{-}(C_5H_5)_2Zr\{Ph_2P(BH_3)N\}_2C_6H_4]$ (**2**), zirconium dichloride complex $[[\{Ph_2P(BH_3)N\}_2C_6H_4]ZrCl_2]$ (**3**), and homoleptic zirconium complex $[[\{Ph_2P(BH_3)N\}_2C_6H_4]_2Zr]$ (**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 chemoselective 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. $CDCl_3$ was distilled and stored in the glovebox. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz), $^{31}P\{^1H\}$ NMR (161.9 MHz), $^{11}B\{^1H\}$ (128.3 MHz), and ^{19}F (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 $[(C_5H_5)_2ZrCl_2]$, 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-ethynyl anisole, methyl 4-ethynylbenzoate, phenylacetylene-D, 4-methylphenylacetylene-D, and 4-bromophenylacetylene-D, were synthesized according to procedures published in the literature.[49]

*Preparation of Ligand $[\{Ph_2P(BH_3)NH\}_2C_6H_4]$ (**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/CH_2Cl_2 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 $[\{Ph_2P(BH_3)NH\}_2C_6H_4]$ (**1-H2**) is soluble in $CDCl_3$, CH_2Cl_2, 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, C_6D_6): δ_H 7.62−7.57 (m, 8H, Ar*H*), 7.39−7.37 (m, 12H, Ar*H*), 7.36−7.18 (m, 2H, Ar*H*), 6.70−6.68 (m, 2H, Ar*H*), 4.52 (d, 2H, J = 4 Hz, N*H*), 1.19 (br, 6H, BH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 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. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 56.0 (d, J = 85.8 Hz) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ_B = −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: $[\{Ph_2P(BH_3)NH\}_2C_6H_4]$ (504.14): calcd (%) C 71.47, H 6.40, N 5.56; found C 71.30, H 6.21, N 5.22.

*Preparation of Complex $[[\{Ph_2P(BH_3)N\}_2C_6H_4]Ti(NMe_2)_2]$ (**1**).* In a 50 mL dry Schlenk flask, ligand **L1-H2** (129 mg, 0.256 mmol) and $Ti(NMe_2)_4$ (40 mg, 0.256 mmol) were mixed together in 10 mL of toluene at an ambient temperature and

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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%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.88−7.83 (m, 8H, Ar*H*), 7.03−6.90 (m, 14H, Ar*H*), 6.53−6.52 (m, 2H, Ar*H*), 3.21 (s, 12H, NMe_2), 2.11 (br, 6H, BH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C = 136.7 (P−ArC), 135.9 (P−ArC), 132.2 (*o*-ArC), 132.1 (*m*-ArC), 128.2 (*p*-ArC), 128.1 (*p*-ArC), 178.9 (ArC), 127.7 (ArC), 45.1 ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ_P 74.1 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ_B = −34.6 (br) ppm. Elemental analysis: $[C_{41}H_{50}B_2N_4P_2Ti]$ (638.1): calcd (%) C 63.99, H 6.63, N 8.78; found C 63.55, H 6.49, N 8.56.

*Preparation of Complex [η^5-$(C_5H_5)_2$Zr{$Ph_2P(BH_3)N$}$_2C_6H_4$] (**2**).* In a 50 mL dry Schlenk flask, a suspension of $ZrCp_2Cl_2$ (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 $LiN(SiMe_3)_2$ (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%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.58−7.57 (m, 6H, Ar*H*), 7.19−6.18 (m, 4H, Ar*H*), 6.99−6.90 (m, 14H, Ar*H*), 6.00 (s, 10H, Cp-*H*), 1.93 (br, 6H, BH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C = 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. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ_P 69.8 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ_B = −35.2 (br) ppm. Elemental analysis: $[C_{40}H_{40}B_2N_2P_2Zr]$ (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 [[{$Ph_2P(BH_3)N$}$_2C_6H_4$]$ZrCl_2$] (**3**).* In a 50 mL dry Schlenk flask, a suspension of $ZrCl_4$ (59.6 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 $LiN(SiMe_3)_2$ (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 (134.4 mg, 0.201 mmol) (79%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.74−7.68 (m, 8H, Ar*H*), 7.05−7.03 (m, 6H, Ar*H*), 6.99−6.97 (m, 10H, Ar*H*), 1.95 (br, 6H, BH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C = 132.6 (P−ArC), 132.5 (P−ArC), 131.7 (*o*-ArC), 129.4 (*m*-ArC), 129.1 (*p*-ArC), 128.4 (*p*-ArC), 128.2 (ArC), 127.9 (ArC) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ_P 66.5 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ_B = −34.9 (br) ppm. Elemental analysis: $C_{30}H_{30}B_2Cl_2N_2P_2Zr$ (662.0): calcd (%) C 54.24, H 4.55, N 4.22; found C 54.07, H 4.23, N 4.03.

*Preparation of Complex [[{$Ph_2P(BH_3)N$}$_2C_6H_4$]$_2$Zr] (**4**).* In a 50 mL dry Schlenk flask, a suspension of $ZrCl_4$ (29.8 mg, 0.128 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 $LiN(SiMe_3)_2$ (85 mg, 0.512 mmol) at an ambient temperature, and the mixture was stirred for 6 h at a temperature of 70 °C. 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 (202.0 mg, 0.187 mmol) (72%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.61−7.56 (m, 8H, Ar*H*), 7.43−7.32 (m, 12H, Ar*H*), 6.73−6.67 (m, 4H, Ar*H*), 1.94 (br, 6H, BH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C = 136.7 (P−ArC), 135.9 (P−ArC), 132.2 (*o*-ArC), 132.1 (*m*-ArC), 128.2 (*p*-ArC), 128.1 (*p*-ArC), 127.9 (ArC), 127.7 (ArC) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ_P 66.9 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ_B = −35.1 (br) ppm. Elemental analysis: $[C_{60}H_{60}B_4N_4P_4Zr]$ (1095.5): calcd (%) C 65.78, H 5.52, N 5.11; found C 65.24, H 5.38, N 5.02.

Preparation of Complex [[{$Ph_2P(BH_3)N$}$_2C_6H_4$]Ti(H)$_2$]. Complex **1** (0.123 mmol) was placed in a 25 mL dry Schlenk flask, to which a solution of 2 equiv of HBpin (0.246 mmol) and 5 mL of toluene was added. We decided to perform the reaction with 2 equiv of HBpin to avoid overlapping signals, as additional equivalents of HBpin could enter the additional titanium core centers. Then, the reaction mixture was stirred at room temperature for 1 h. After that, the color of the solution faded. The solvent was evaporated in vacuo to obtain a light yellow residue, which was washed twice with *n*-hexane (2 × 5 mL) to remove excess HBpin. The title compound was recrystallized from toluene at −35 °C. Yield: (85 mg, 0.153 mmol) (92%). ^{1}H NMR (400 MHz, C_6D_6): δ_H = 7.30−7.27 (m, 1H, Ar*H*), 7.25−7.19 (m, 5H, Ar*H*), 7.18−7.14 (m, 6H, Ar*H*), 2.76 (s, 6H, NMe_2), 2.25 (s, 3H, BH_3), 1.26 (s, 12H, CH_3) ppm; ^{13}C NMR (100 MHz, C_6D_6): δ_C = 137.7, 129.2, 128.4, 28.2, 127.9, 127.7, 125.6, 82.1, 36.4, 24.8, 21.4 ppm; ^{31}P NMR (161.9 MHz, C_6D_6): δ_P = 69.3 ppm; ^{11}B NMR (128.4 MHz, C_6D_6): δ_B = 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 placed 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 ^{1}H NMR spectroscopy using hexamethylbenzene (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** was 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 F^2 by full-matrix least-

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squares methods, using SHELXL-2016/6.[51] Nonhydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum||Fo| - |Fc||)/\sum|Fo|$ and $[\sum w(Fo^2 - Fc^2)^2/\sum(wFo^4)]^{1/2}$, 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).

■ ASSOCIATED CONTENT

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}, ^{11}B{^{1}H}, NMR spectra, mass spectra, and combustion analyses of all (*E*)-alkenyl boranes, diboronate 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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Author Contributions

†J.B. and A.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Yoon, C. H.; Yoo, K. S.; Yi, S. W.; Mishra, R. K.; Jung, K. W. Oxygen-Promoted Palladium(II) Catalysis: Facile C(sp^2)−C(sp^2) Bond Formation via Cross-Coupling of Alkenylboronic Compounds and Olefins. *Org. Lett.* **2004**, *6*, 4037−4039. (b) Yang, M.; Yokokawa, N.; Ohmiya, H.; Sawamura, M. Synthesis of Conjugated Allenes through Copper-Catalyzed γ-Selective and Stereospecific Coupling between Propargylic Phosphates and Aryl- or Alkenylboronates. *Org.Lett.* **2012**, *14*, 816−819. (c) Tonogaki, K.; Itami, K.; Yoshida, J. Sequential Pd- and Rh-Catalyzed Three-Component Cyclization with Allenylboronate Platform. *Org. Lett.* **2006**, *8*, 1419−1422. (d) Ueno, S.; Chatani, N.; Kakiuchi, F. Regioselective Alkenylation of Aromatic Ketones with Alkenylboronates Using a $RuH_2(CO)(PPh_3)_3$ Catalyst via Carbon−Hydrogen Bond Cleavage. *J. Org. Chem.* **2007**, *72*, 3600−3602. (e) de la Herrán, G.; Mba, M.; Murcia, M. C.; Plumet, J.; Csaky, A. G. Stereoselectivity Control in the Rh(I)-Catalyzed Conjugate Additions of Aryl and Alkenylboronic Acids to Unprotected Hydroxycyclopentenones. *Org. Lett.* **2005**, *7*, 1669−1671. (f) Hatakeyama, T.; Nakamura, M.; Nakamura, E. Diastereoselective Addition of Zincated Hydrazones to Alkenylboronates and Stereospecific Trapping of Boron/Zinc Bimetallic Intermediates by Carbon Electrophiles. *J. Am. Chem. Soc.* **2008**, *130*, 15688−15701. (g) Itami, K.; Tonogaki, K.; Ohashi, Y.; Yoshida, J. Rapid Construction of Multisubstituted Olefin Structures Using Vinylboronate Ester Platform Leading to Highly Fluorescent Materials. *Org. Lett.* **2004**, *6*, 4093−4096.

(2) Hall, D. G. *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*;Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2011.

(3) Torborg, C.; Beller, M. Recent Applications of Palladium-Catalyzed Coupling Reactions in the Pharmaceutical, Agrochemical, and Fine Chemical Industries. *Adv. Synth. Catal.* **2009**, *351*, 3027−3043.

(4) (a) Hartwig, J. F. Borylation and Silylation of C−H Bonds: A Platform for Diverse C−H Bond Functionalizations. *Acc. Chem. Res.* **2012**, *45*, 864−873. (b) Lennox, A. J.; Lloyd-Jones, G. C. Selection of boron reagents for Suzuki−Miyaura coupling. *Chem. Soc. Rev.* **2014**, *43*, 412−443.

(5) Mahrwald, R., Ed. *Modern Aldol Reactions*; Wiley-VCH: Weinheim, 2010.

(6) Cordova, A., Ed. *Catalytic Asymmetric Conjugate Reactions*; WileyVCH: Weinheim, 2010.

(7) de Vries, J. G.; Elsevier, C. J., Eds. *The Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, 2007.

(8) Oro, L. A.; Carmona, D.; Fraile, J. M. In *Metal-Catalysis in Industrial Organic Processes*; Chiusoli, G. P.; Maitlis, P. M., Eds.; RSC Publishing: London, 2006; pp 79−113.

(9) Eller, K.; Henkes, E.; Rossbacher, R.; Hoke, H. Aliphatic Amines. *Ullmann's Encyclopedia of Industrial Chemistry*; 7th ed.; Wiley-VCH: Weinheim, Germany, 2008; Vol. *A2*, p 2.

(10) (a) Lawrence, S. A. *Amines: Synthesis, Properties, and Application*; Cambridge University: Cambridge, 2004. (b) Eller, K. et al. Aliphatic Amines. *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-VCH: Weinheim, Germany, 2008; Vol. *A2*, p 2.

(11) (a) Nakajima, K.; Kato, T.; Nishibayashi, Y. Hydroboration of Alkynes Catalyzed by Pyrrolide-Based PNP Pincer Iron Complexes. *Org. Lett.* **2017**, *19*, 4323−4326. (b) Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Kohn, G.; Liptrot, D. J.; Mahon, M. F. Magnesium-catalysed nitrile hydroboration. *Chem. Sci.* **2016**, *7*, 628−641. (c) Stachowiak, H.; Kaźmierczak, J.; Kuciński, K.; Hreczycho, G. Catalyst-Free and Solvent-Free Hydroboration of Aldehydes. *Green Chem.* **2018**, *20*, 1738−1742.

(12) Nakajima, K.; Kato, T.; Nishibayash, Y. Hydroboration of Alkynes Catalyzed by Pyrrolide-Based PNP Pincer−Iron Complexes. *Org. Lett.* **2017**, *19*, 4323−4326.

(13) Ben-Daat, H.; Rock, C. L.; Flores, M.; Groy, T. L.; Bowman, A. C.; Trovitch, R. J. Hydroboration of alkynes and nitriles using an α-diimine cobalt hydride catalyst. *Chem. Commun.* **2017**, *53*, 7333−7336.

(14) (a) Lee, J. E.; Kwon, J.; Yun, J. Copper-catalyzed addition of diboron reagents to α,β-acetylenic esters: efficient synthesis of β-boryl-α,β-ethylenic esters. *Chem. Commun.* **2008**, 733−734. (b) Kim, H. R.; Jung, I. G.; Yoo, K.; Jang, K.; Lee, E. S.; Yun, J.; Son, S. U. *Chem. Commun.* **2010**, *46*, 758−760. (c) Kim, H. R.; Yun, J. Highly regio- and stereoselective synthesis of alkenylboronic esters by copper-catalyzed boron additions to disubstituted alkynes. *Chem. Commun.* **2011**, *47*, 2943−2945.
(15) Prechtl, M. H. G.; Ben-David, Y.; Giunta, D.; Busch, S.; Taniguchi, Y.; Wisniewski, W.; Görls, H.; Mynott, R. J.; Theyssen, N.; Milstein, D.; Leitner, W. Synthesis and Characterisation of Non-classical Ruthenium Hydride Complexes Containing Chelating Bidentate and Tridentate Phosphine Ligands. *Chem. − Eur. J.* **2007**, *13*, 1539−1546.
(16) Zaidlewicz, M.; Wolan, A.; Budny, M. In *Hydrometallation of C−C and C−C Bonds. Group 3*, 2nd ed.; Knochel, P.; Molander, G. A., Eds.; Elsevier: Amsterdam, 2014.
(17) Tamang, S. R.; Findlater, M. Iron Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2017**, *82*, 12857−12862.
(18) Evans, D. A.; Fu, G. C. The rhodium-catalyzed hydroboration of olefins: a mechanistic investigation. *J. Org. Chem.* **1990**, *55*, 2280−2282.
(19) Arévalo, R.; Vogels, C. M.; MacNeil, G. A.; Riera, L.; Pérez, J.; Westcott, S. A. Rhenium-catalysed hydroboration of aldehydes and aldimines. *Dalton Trans.* **2017**, *46*, 7750−7757.
(20) Chen, S.; Yan, D.; Xue, M.; Hong, Y.; Yao, Y.; Shen, Q. Tris(cyclopentadienyl)lanthanide Complexes as Catalysts for Hydroboration Reaction toward Aldehydes and Ketones. *Org. Lett.* **2017**, *19*, 3382−3385.
(21) Oluyadi, A. A.; Ma, S.; Muhoro, C. N. Titanocene(II)-Catalyzed Hydroboration of Carbonyl Compounds. *Organometallics* **2013**, *32*, 70−78.
(22) Wang, W.; Shen, X.; Zhao, F.; Jiang, H.; Yao, W.; Pullarkat, S. A.; Xu, L.; Ma, M. Ytterbium-Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83*, 69−74.
(23) Guo, J.; Chen, J.; Lu, Z. Cobalt-catalyzed asymmetric hydroboration of aryl ketones with pinacolborane. *Chem. Commun.* **2015**, *51*, 5725−5727.
(24) Li, J.; Luo, M.; Sheng, X.; Hua, H.; Yao, W.; Pullarkat, S. M.; Xu, L.; Ma, M. Unsymmetrical β-diketiminate magnesium(I) complexes: syntheses and application in catalytic hydroboration of alkyne, nitrile and carbonyl compounds. *Org. Chem. Front.* **2018**, *5*, 3538−3547.
(25) Deng, C. M.; Ma, Y. F.; Wen, Y. M. Transition-Metal-Free Borylation of Alkynes and Alkenes. *ChemistrySelect* **2018**, *3*, 1202−1204.
(26) Bismuto, A.; Thomas, S. P.; Cowley, M. J. Aluminum Hydride Catalyzed Hydroboration of Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 15356−15359.
(27) Bismuto, A.; Thomas, S. P.; Cowley, M. J. Aluminum-Catalyzed Hydroboration of Alkenes. *ACS Catal.* **2018**, *8*, 2001−2005.
(28) (a) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. J. An Aluminum Dihydride Working as a Catalyst in Hydroboration and Dehydrocoupling. *J. Am. Chem. Soc.* **2016**, *138*, 2548−2551. (b) Franz, D.; Sirtl, L.; Pothig, A.; Inoue, S. Aluminum Hydrides Stabilized by N-Heterocyclic Imines as Catalysts for Hydroborations with Pinacolborane. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245−1250.
(29) Seyden-Penne, J. *Reductions by Alumino and Borohydrides in Organic Synthesis*, 2nd ed.; Wiley-VCH: New York, 1997.
(30) Saleh, H. E.-D. M.; Koller, M. Introductory Chapter: Principles of Green Chemistry. *Green Chemistry*; IntechOpen, 2018.
(31) Ryken, S. A.; Schafer, L. L. *N,O*-Chelating Four-Membered Metallacyclic Titanium(IV) Complexes for Atom-Economic Catalytic Reactions. *Acc. Chem. Res.* **2015**, *48*, 2576−2586.
(32) Haynes, W. M. *CRC Handbook of Chemistry and Physics: A Readyreference Book of Chemical and Physical Data*, 94th ed.; Taylor & Francis: Boca Raton, FL, 2013−2014.
(33) Wang, D.; Astruc, D. The recent development of efficient Earth-abundant transition-metal nanocatalysts. *Chem. Soc. Rev.* **2017**, *46*, 816−854.
(34) Su, B.; Cao, Z. C.; Shi, Z. J. Exploration of Earth-Abundant Transition Metals (Fe, Co, and Ni) as Catalysts in Unreactive Chemical Bond Activations. *Acc. Chem. Res.* **2015**, *48*, 886−896.
(35) Harinath, A.; Bhattacharjee, J.; Panda, T. K. Catalytic Hydroboration of Organic Nitriles Promoted by Aluminum Complex. *Adv. Synth. Catal.* **2019**, *361*, 850−857.
(36) He, X. M.; Hartwig, J. F. True Metal-Catalyzed Hydroboration with Titanium. *J. Am. Chem. Soc.* **1996**, *118*, 1696−1702.
(37) Motry, D. H.; Smith, M. R., III Facile, Metal-Mediated Dehydrogenative Borylation of Ethylene: Selective Conversion of a Titanium-Bound Olefin to a Vinylboronate Ester. *J. Am. Chem. Soc.* **1995**, *117*, 6615−6616.
(38) Motry, D. H.; Brazil, A. G.; Smith, M. R., III Significance of Borane Tuning in Titanium-Catalyzed Borylation Chemistry. *J. Am. Chem. Soc.* **1997**, *119*, 2743−2744.
(39) Pereira, S.; Srebnik, M. Hydroboration of Alkynes with Pinacolborane Catalyzed by HZrCp2Cl. *Organometallics* **1995**, *14*, 3127−3128.
(40) Bhattacharjee, J.; Harinath, A.; Banerjee, I.; Nayek, H. P.; Panda, T. K. Highly Active Dinuclear Titanium(IV) Complexes for the Catalytic Formation of a Carbon−Heteroatom Bond. *Inorg. Chem.* **2018**, *57*, 12610−12623.
(41) Bhattacharjee, J.; Das, S.; Kottalankaa, R. K.; Panda, T. K. Hydroamination of carbodiimides, isocyanates, and isothiocyanates by a bis(phosphinoselenoic amide) supported titanium(IV) complex. *Dalton Trans.* **2016**, *45*, 17824−17832.
(42) Kottalanka, R. K.; Anga, S.; Naktode, K.; Laskar, P.; Nayek, H. P.; Panda, T. K. Amidophosphine−Borane Complexes of Alkali Metals and the Heavier Alkaline-Earth Metals: Syntheses and Structural Studies. *Organometallics* **2013**, *32*, 4473−4482.
(43) Bhattacharjee, J.; Harinath, A.; Sarkar, A.; Panda, T. K. Polymerization of ε-Caprolactam to Nylon-6 Catalyzed by Barium σ-Borane Complex under Mild Condition. *ChemCatChem* **2019**, *11*, 3366−3370.
(44) (a) Wiecko, M.; Girnt, D.; Rastätter, M.; Panda, T. K.; Roesky, P. W. Zirconium complexes having a chiral phosphanylamide in the co-ordination sphere. *Dalton Trans.* **2005**, 2147. (b) Naktode, K.; Kottalanka, R. K.; Panda, T. K. N-(2,6-Dimethylphenyl)-diphenylphosphinamine chalcogenides (S, Se) and a zirconium complex possessing phosphanylamide in the coordination sphere. *New J. Chem.* **2012**, *36*, 2280.
(45) Mandal, S.; Vermaa, P. K.; Geetharani, K. Lewis acid catalysis: regioselective hydroboration of alkynes and alkenes promoted by scandium triflate. *Chem. Commun.* **2018**, *54*, 13690−13693.
(46) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. Ruthenium Catalyzed Hydroboration of Terminal Alkynes to *Z*-Vinylboronates. *J. Am. Chem. Soc.* **2012**, *134*, 14349−14352.
(47) Harinath, A.; Bhattacharjee, J.; Gorantla, K. R.; Mallik, B. S.; Panda, T. K. Hydroboration, Cyanosilylation, and Sequential Cyanosilylation and Hydroboration of Carbonyl Compounds in the Presence of a Ti^{IV} Amido Complex as an Efficient Catalyst. *Eur. J. Org. Chem.* **2018**, 3180−3192.
(48) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. An Aluminum Hydride That Functions like a Transition-Metal Catalyst. *Angew. Chem., Int. Ed.* **2015**, *54*, 10225−10229.
(49) Yabe, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. Site-Selective Deuterated-Alkene Synthesis with Palladium on Boron Nitride. *Chem. − Eur. J.* **2013**, *19*, 484−488.
(50) (a) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. Completion and Refinement of Crystal Structures with SIR92. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2004: An Improved Tool for Crystal Structure Determination and Refinement. *J. Appl. Crystallogr.* **2005**, *38*, 381.

https://dx.doi.org/10.1021/acsomega.9b03598
ACS Omega XXXX, XXX, XXX−XXX

(51) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.

https://dx.doi.org/10.1021/acsomega.9b03598
ACS Omega XXXX, XXX, XXX−XXX