An “On-Demand”, Selective Dehydrogenative Borylation or Hydroboration of Terminal Alkynes Using Zn$^{2+}$-based Catalyst

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An air-stable dicationic Zn$^{2+}$ complex (1) in a tripod-type ligand with non-bound phosphorus base and three pyridinyl “arms” (TPPh) was synthesized. Remarkably, while 2 mol% of 1 at room temperature selectively catalyzed dehydrogenative borylation of terminal alkynes with HBPin, a lower loading of 1 (0.5 mol%) at 90 °C selectively promoted hydroboration reaction of the same alkynes skipping the dehydrogenative borylation step. The mode of action of 1 was proposed based on experimental observations as well as the mechanism of dehydrogenative borylation was studied by DFT computations.

Introduction

Organoboranes are highly valuable compounds in a variety of chemical transformations and often regarded as key building blocks for molecules with applications ranging from materials to life sciences.[1] Therefore, the development of new and efficient methods to synthesize new organoborane compounds still remains a point of interest. Classical methods to synthesize organoboranes include the transmetalation from organolithium or organomagnesium reagents. These methods, however, have their drawbacks: a) organolithium and organomagnesium precursors have to be prepared, which adds additional steps to the synthesis; b) organolithium and organomagnesium are highly reactive which makes them intolerant to functional groups; c) this methodology produces a lot of waste material and thus has poor atom economy. Consequently, the need for more convenient methods for the preparation of organoboranes led, in the last decade, to the discovery of a number of catalytic methods for incorporation of a boron into organic molecules using mostly commercially available pinacolborane (HBPin) or bis(pinacolato)diboron (B$_2$Pin$_2$) (Scheme 1). The catalytic processes through which the organoboranes are usually obtained are the hydroboration of C=C double and C≡C triple bonds, and dehydrogenative borylation of Ar–H bonds or R–C=C–H bonds in terminal alkynes.[2]

Scheme 1. Examples of hydroboration and dehydrogenative borylation reactions: with transition metals (A), zinc catalysts (B) and current work (C).

Unlike numerous examples of the catalytic hydroboration of alkynes (C≡C) that can be done with a variety of different transition metal and transition metal-free catalysts, the catalytic dehydrogenative borylation of terminal alkynes is less established and only a handful number of examples was reported to date (Scheme 1A and 1B). For example, the first dehydrogenative borylation of terminal alkyne catalyzed by Ir-based complex was discovered by Ozerov and co-workers eight years ago.[3] Later, in 2017, Bertrand’s group showed cyclic (alkyl) (amino)carbene (cAAC) Cu salt capable of doing similar chemistry.[4] In 2018, Darcel reported the catalytic dehydrogenative borylation of terminal alkynes using Fe(OTf)$_2$ (Scheme 1A).[5]

Zn-based compounds have recently attracted a lot of attention due to their catalytic activity in hydroboration and dehydrogenative borylation of terminal alkynes (Scheme 1B).
Uchiyama reported in 2013 a hydroboration of C≡C triple bonds using Et₂Zn and B₂Pin. Later, Geetharani reported hydroboration reaction of alkynes using catalytic amounts of Zn(OTf)₂ and [Na][HBEt]₂. Tsuchimoto showed that the catalytic dehydrogenative borylation of alkynes could be achieved by Zn(OTf)₂. Ingleson recently reported the dehydrogenative borylation of alkynes catalyzed by N-heterocyclic carbene (NHC) Zn cation adducts (NHC–Zn⁺), remarkably this catalyst could further hydroborate the resulting alkynyl boronate giving di- and tri-borylated compounds. Ma, in 2021, showed that similar reaction sequence (dehydroborylation followed by hydroboration) could be catalyzed by ZnBr₂ (Scheme 1B).³⁶

It is important to note that all of the catalytic systems known up to date (Scheme 1A and 1B), to the best of our knowledge, selectively catalyze either the hydroboration or C–H dehydrogenative borylation of terminal alkynes. As previously mentioned, Ingleson and Ma showed Zn-based systems that sequentially catalyze dehydrogenative borylation followed by hydroboration (Scheme 1B), however, in both these cases the reaction is dominated by dehydrogenative borylation, therefore, skipping this step and obtaining the mono-hydroboration product was not shown. Thus, developing a catalytic system which could “on-demand” selectively promote either dehydrogenative borylation or hydroboration is interesting and highly desirable.

Here we report an air-stable, dicaticonic zinc-based complex, [TPhPZn⁺⁺][BF₄]₂ (1) that could selectively catalyze dehydrogenative borylation at r.t. with 2 mol% catalyst loading, while 0.5 mol% of 1 at 90 °C promoted the hydroboration reaction, remarkably skipping the dehydrogenative borylation step (Scheme 1C).

Results and Discussion

Recently we reported an air-stable, di-cationic zinc complex in tridentate tris(2-methyl-6-pyridylmethyl) phosphine (TmPPh) hemilabile ligand (1a) (Scheme 2) that was found to be an efficient catalyst for the hydrosilylation of unsaturated C–C and C=C triple bonds, and interestingly was inactive in hydrosilylation of C≡C (E = O, N) bonds. One of the major drawbacks of this Zn-based catalyst was the fact that it required high temperatures (120–140 °C) to be active in these hydrosilylation reactions. Two factors were suspected in causing 1a to be inactive at lower temperatures: one is the steric hindrance around the Lewis acidic Zn²⁺ center, and two, is the strong electron donating effect of the lutidinyl based arms, somewhat quenching the Lewis acidic Zn center. To solve this issue and achieve better catalytic activity i.e. lower working temperature, we decided to use a less sterically encumbered and less electron donating ligand with pyridinyl “arms”, tris(6-pyridylmethyl) phosphine (TPPh). To synthesize dicaticonic Zn-based complex 1. Thus, similarly to the previously reported 1a, the reaction of TPPh with ZnCl₂ followed by the abstraction of two Cl⁻ anions by two equiv. of K[BF₄] led to the desired 1 (Scheme 2). Similarly to 1a, Zn²⁺ center in 1 is coordinatively bound to three pyridinyl “arms”, while the phosphorus base of the ligand is inverted away from Zn²⁺ center, meaning that the lone pair at P-center face the opposite direction from Zn²⁺ center. This can be clearly concluded from the ⁳¹P-NMR chemical shift of 1 which is similar to free TPhP (δ = −12 ppm) (see ESI, for the molecular structure of 2). Repeated efforts to obtain suitable crystals of 1 for single crystal X-ray analysis were not successful, however, its formulation could be well corroborated by multinuclear NMR and mass spectrometry.

The catalytic activity of 1 was first tested in hydrosilylation reactions of alkenes and alkynes. As expected, 1 was an active catalyst for the hydrosilylation reaction at lower temperatures (50–70 °C) compared to its predecessor 1a. However, it is worth noting that the improved reactivity of 1 came at the expense of catalyst selectivity. In contrast to our previously reported Zn-based complex (1a) that was inactive catalyst in hydrosilylation of carbonyls, 1 (0.5 mol%) catalyzed the hydrosilylation reaction of both C–C and C≡E (E = O, N) double bonds. The higher reactivity of 1 encouraged us to examine other catalytic hydroelementation reactions. We first decided to test the possibility of 1 to catalyze the hydroboration reaction of alkynes. Thus, to a solution of HBPin and phenylacetylene in 1,2-difluorobenzene (o-DFB) a catalytic amount of 1 (2 mol%) was added at room temperature (Table 1, entry 1). Immediately after addition of 1, gas evolution was observed, ¹H NMR analysis after 15 min. of the reaction showed full consumption of phenylacetylene and no formation of the hydroboration product, Ph(H)C≡C(H)HBPin (4). A closer look at the ¹H NMR and Ph(H)C≡C(H)HBPin (4). A closer look at the ¹H NMR and ¹³C NMR analysis of the reaction mixture showed the presence of a highly enriched diborylated product 2b.

![Scheme 2. Synthesis of dicaticionic zinc complex 1.](image-url)

| Entry | Cat. [mol%] | Temp. | time [h] | 3 [%] | 4 [%] |
|-------|------------|-------|----------|-------|-------|
| 1     | 2          | RT    | 0.25     | 99%   | -     |
| 2     | 0.5        | RT    | 150      | ~95%  | ~5%   |
| 3     | 0.5        | 90 °C | 20       | ~20%  | ~80%  |
| 4[a]  | 0.5        | 90 °C | 20       | -     | 99%   |

[a] Phenylacetylene is added after short preheating of 1 (0.5 mol%) and HBPin, or Phenylacetylene, 1 (0.5 mol%) and HBPin are mixed at 5–10 °C and then heated to 90 °C.
\[ ^{13} \text{C NMR spectra revealed the formation of the dehydrogenative borylation coupling product of phenylacetylene, P}-C=C-BPin (3) (Table 1, entry 1). To optimize the conditions of this catalysis, we performed the same reaction with a lower catalyst loading of 0.5 mol\% (Table 1, entry 2). As a consequence, the reaction rate greatly decreased and only after 150 h the reaction reached full conversion to dehydroborylation product 3 (~95\%) and ~5\% of initially expected anti-Markovnikov, \( E \) isomer hydroboration product 4 (Table 1, entry 2). To increase the reaction rate the reaction mixture of HBPin, phenylacetylene and 1 (0.5 mol\%) in \( o \)-DFB was heated to 90 °C (Table 1, entry 3). To our surprise, heating the reaction drastically changed its course, previously minor product 4 became a major product (~80\%) and 3 was formed as minor product (~20\%) after 20 h of heating (Table 1, entry 3). Interestingly, when 1 was mixed with HBPin in \( o \)-DFB and heated (~90 °C) for ~10 min. and only after phenylacetylene was added to this mixture and the reaction heated to 90 °C for 20 h, resulted in formation of hydroboration product 4 only (Table 1, entry 4). Importantly, longer preheating of 1 and HBPin resulted in a non-reactive catalytic system. Similar result could be obtained when all three components of the reaction 1 (0.5 mol\%), HBPin and alkyne were mixed at low temperature (5–10 °C) and then directly heated to 90 °C (Table 1, entry 4).

Surprisingly, 1a did not produce any reactivity in these reactions, meaning that even slight structural change in these \( \text{Zn}^{2+} \) cations leads to a great difference in their chemistry.

The ability of 1 to selectively promote the reaction in two different directions, dehydrogenative borylation or hydroboration, depending only on the reaction conditions is remarkable, and to the best of our knowledge such activity was not reported previously for a single catalytic system.

After finding that by using complex 1 we can selectively navigate between two different reaction routes, we moved to examine this methodology on a broader scope of terminal alkynes. First, we focused on the dehydrogenative borylation reaction. As previously shown, the optimal conditions for this reactions’ direction was using 2 mol\% of 1 at r.t. (Table 1, entry 1). Thus, using these optimal conditions the reactions between a variety of terminal alkynes and HBPin in presence of 1 (2 mol\%) was carried out. 4-Ethynyltoluene similarly to phenylacetylene after 1 h gave cleanly the borylated product 3a (Table 2). Alkynes with the electron-withdrawing groups at the aryl attached to C\( _n \)N\( _n \)C triple bond, expectedly, required more time for full conversion to the dehydroborylation coupling products (Table 2, 3b–3d). Surprisingly, alkynes with an electron-donating groups at the aryl ring also required longer reaction times, despite the fact that these C\( _n \)C triple bonds are more electron rich (Table 2, 3e–3g). This possibly can be explained by the coordination of the heteroatoms (O, N) in these molecules to the Lewis acidic \( \text{Zn}^{2+} \) center in 1, somewhat quenching its reactivity. Dehydrogenative borylation of alkyl acetylenes was also successfully catalyzed by 1, however, again longer reaction times compared to phenylacetylene were required for full conversion (Table 2, 3h–3l). Remarkably, this method was tolerant towards an alkyl chloride moiety in 3k, which remained intact as well as selective towards dehydrogenative borylation of the terminal alkyne moiety over hydroboration of the C\( _n \)C double bond in enyne 3l (Table 2). The reaction with trimethylsilylacetylene expectedly led to 3m in high yields. Interestingly, the reaction with 3-butyn-1-ol led to doubly dehydrogenative borylation product, 3l. Notably, in contrast to previously reported dehydrogenative coupling reaction by Tsuchimoto,\(^\text{[7]}\) this catalytic reaction was compatible with HBPin and did not require heating.

Next we tested the hydroboration reaction on a larger scope of terminal alkynes. Thus, a mixture of 1 (0.5 mol\%) and HBPin (1.2 equiv.) in \( o \)-DFB was heated to ~90 °C for ~10 min. and right after terminal alkynes were added (1 equiv.), and this mixture was further heated to 90 °C, and the progress of the reaction was monitored by NMR spectroscopy. Hydroboration reactions of terminal alkynes in most cases required long (20 h) reaction times (Table 3). Both electron-donating and electron-withdrawing groups at the aryl ring attached to C\( _n \)C triple bond did not have a significant effect on the reaction times, and hydroboration products (4b–4f) were formed after 20 h (Table 3). Unlike dehydrogenative borylation reaction of 4-ethylbenzonitrile which cleanly led to 3c, the hydroboration

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**Table 2. Dehydrogenative borylation of terminal alkynes catalyzed by 1**

| Entry | Alkyne | Product | Time (h) |
|-------|--------|---------|----------|
| 1 | 4-ethylbenzonitrile | 3a | 20 |
| 2 | 3-butyn-1-ol | 3l | 15 |
| 3 | 3-hexyne | 3m | 90 |
| 4 | Trimethylsilylethynylbenzonitrile | 3k | 10 |
| 5 | 3-pentyn-1-ol | 3l | 30 |
| 6 | 3-hexyn-1-ol | 3l | 60 |

\(^{a}\) To a 1:1.05 solution of alkyne and HBPin in \( o \)-DFB. 1 (2 mol\%) was added and the reaction mixture was stirred for the indicated period of time; \(^{b}\) NMR yields (isolated yields) are reported.
reaction was not that selective and led to a mixture of products, possibly due to hydroboration of the C\(\equiv\)N triple bond along with C\(\equiv\)C triple bond. Alkyl acetylenes also worked in this hydroboration reaction, all giving alkene boronates in high yields. In 1-ethynylcyclohexene the hydroboration occurred solely on the C\(\equiv\)C triple bond giving 4\(i\) (Table 3), while the C\(=\)C double bond remained untouched. Interestingly, trimethylsilylacetylene reacted in hydroboration reaction leading to a 1:1 mixture of trans- and gem- double bonds 4\(k\) (Table 3). The hydroboration of the reaction with 3-butyln-1-ol did not produce a clean reaction and led to a complex mixture of products.

Noteworthy, similarly to previously reported\(^{[9a]}\), the diborylation of terminal alkynes through sequential dehydrogenative borylation followed by hydroboration reaction could also be achieved (see ESI for more details). Importantly, changing the reaction sequence to first hydroboration followed by dehydrogenative coupling did not work and led only to hydroboration products.

Before trying to understand the mechanism of the reaction and the origin of the difference in reactivity of 1 under different conditions (dehydrogenative borylation vs. hydroboration), we would like to emphasize a number of experimental observations:

1. When 1 is mixed with excess of HBPin in 1:2 ratio the reaction takes place leading to a number of unidentified products as can be observed by \(^{31}\)P NMR. Along with the change in NMR, a greyish powder material precipitates out of a solution, which presumably is ZnH\(_2\) (Scheme 3a).

2. In the catalytic dehydrogenative borylation reaction, if the reaction is done with a slight excess of alkyne, in the end of the catalysis 1 can be still detected by NMR (Scheme 3b).

3. In the end of the hydroboration reaction of alkynes 1 can no longer be detected by NMR, but a similar picture to the reaction of 1 with HBPin only can be observed by \(^{31}\)P NMR (Scheme 3c).

4. The two catalytic reactions are switchable only in one direction i.e., catalytic hydroboration of terminal alkynes is possible after dehydrogenative borylation, however, once the reaction is heated for the hydroboration reaction the dehydrogenative borylation of terminal alkynes no longer works (Scheme 3d).

Based on these experimental observations, we propose the following mechanistic picture. In the dehydrogenative borylation reaction, 1 first activates H-BPin bond in a frustrated Lewis pairs (FLPs)\(^{[13]}\) type manner between the Lewis acidic Zn-center and Lewis basic pyridine arm, which is similar to the previously reported by us activation of Si\(\equiv\)H bond,\(^{[10]}\) leading to intermediate Int\(_1\) (Scheme 4a, path i). Int\(_1\) then reacts with terminal alkyne eliminating H\(_2\) producing zinc acetylide species Int\(_2\) (Scheme 4a, path ii). Zinc acetylide moiety is then borylated by the PinB group attached to N-center in Int\(_2\), forming a complex between alkynyl boronate, the product of this catalytic reaction, and Zn and N centers (Int\(_3\)) (Scheme 4a, path iii). The alkynyl boronate in Int\(_3\) is then replaced by another molecule of HBPin, regenerating Int\(_1\) (Scheme 4a, path iv).

The first step of the hydroboration reaction is competing with the dehydrogenative borylation reaction described above. Thus, we believe that 1, when reacted with HBPin, decomposes leading to ZnH\(_2\) and an unidentified mixture of cationic borenium-type species ([L·BP\(\text{in}\)]\(^+\)) (Scheme 4b). A similar reactivity of organozinc species with hydroboranes was reported recently\(^{[14]}\). These [L·BP\(\text{in}\)]\(^+\) species, rather than 1, are the actual catalyst in the hydroboration reaction of terminal alkynes, and do not catalyze the dehydrogenative borylation

### Table 3. Hydroboration of terminal alkynes promoted by 1\(^{[a,b]}\)

| R          | H      | 1.2 HBPin | o-DPB, 90 °C | R          | H      | BPin |
|------------|--------|-----------|--------------|------------|--------|------|
| H          |        |           |              | H          |        |      |
| H          |        |           |              | H          |        | BPin |
| 4\(a\)     | 99% (95%), 10 h |          |              | 4\(b\)     | 99% (89%), 20 h |
| 4\(c\)     | 99% (80%), 20 h |          |              | 4\(d\)     | 99% (82%), 20 h |
| 4\(e\)     | 99% (80%), 20 h |          |              | 4\(f\)     | 99% (85%), 20 h |
| 4\(g\)     | 99% (80%), 20 h |          |              | 4\(h\)     | 99% (70%), 20 h |

\(^a\) A Schlenk flask was charged with 1.2 equivalent HBPin and 1 (0.5 mol %) in o-DPB. The mixture was heated for ~10 min; at 90 °C before addition of 1 equiv of alkyne and further heated at 90 °C for indicated period of time; \(^b\) NMR yields (isolated yields) are reported.

### Scheme 3. Experimental observations of the reaction between 1, HBPin, and PhC\(\equiv\)C–H under different conditions.
reaction at all (Scheme 4b). This mechanistic picture could explain the experimental observations that were described above and the fact the dehydrogenative borylation requires higher catalyst loading than the hydroboration reaction. Thus, due to competition of the two reactions at r.t., dehydroborolation vs. decomposition of 1 and formation of [L · BPin]+, high catalyst (1) loading (2 mol%) is enough to promote the dehydrogenative borylation reaction up to full conversion before 1 is fully transformed to [L · BPin]+ that is no longer active in this catalytic reaction. On the other hand, when low catalyst (1) loading (0.5 mol%) is used and the reaction is heated, 1 rapidly decomposes in presence of large excess of HBPin producing [L · BPin]+ before the dehydroborylation reaction takes place to a significant amount. This can also explain the fact that these two reactions are not switchable, and once heated only the hydroboration reaction works, since heating increases the rate of decomposition of 1 to [L · BPin]+.

This is also why a short preheating of 1 and HBPin (Table 1, entry 4) before the addition of alkynes gives the best hydroboration results, with no boronato alkyne formation at all. Additionally, we reacted 1 with HBPin and heated it to 90°C for 10 min. as expected the grey powder (presumably ZnH₂) was formed. The powder was then separated from the solution and two independent catalytic hydroboration reactions of phenylacetylene were performed. The first reaction was with the soluble part containing what we believe to be [L · BPin]+ species as catalyst, while the second reaction was using the powder (ZnH₂). As result, only the first catalytic reaction produced product 4 (Table 3), in contrast, the reaction with powder did not lead to any reactivity and phenylacetylene remained intact. These experimental observations further supported our hypothesis regarding the nature of the catalyst ([L · BPin]+) in hydroboration reactions (see ESI for details).

To further support the suggested mechanism of dehydrogenative borylation reaction (Scheme 4a) density functional theory (DFT) calculations were performed in the gas phase of the reaction between Me–C=CH and HBPin* (1,3,2-dioxaborolane) catalyzed by 1, using the BP86 method, with Ahlrichs' def2-SVP basis set and with the relativistic effect of zinc, which was accounted for by the Stuttgart-Dresden (SDD) effective core potential (ECP). Based on these calculations, the first step of the catalytic dehydroborylation, which is an FLP-type cleavage of an H–B bond between Lewis acidic Zn and Lewis basic N centers leading to Int1 is strongly exergonic and exothermic with ΔG and ΔH of −21.9 and −30.0 kcal · mol⁻¹, respectively (Scheme 4a, path i). The next proposed step of this catalytic cycle, the deprotonation of the Me–C=CH by ZnH moiety in Int1 leading to zinc acetylide (Int2) and evolution of H₂ is also exergonic (ΔG = −9.3 kcal · mol⁻¹) and exothermic (ΔH = −11.8 kcal · mol⁻¹) (Scheme 3a, path iii). Noteworthily, intensive H₂ evolution was observed right after the addition of 1 to the reaction mixture. H₂ was also measured by ¹H NMR (δ = 4.8 ppm). The third step of the proposed mechanism, a rearrangement leading to boronato alkyne that is simultaneously bound to zinc and nitrogen centers (Int3) is both exergic and exothermic (ΔG = −5.7 and ΔH = −10.3 kcal · mol⁻¹) (Scheme 4a, path iii). The last step of the proposed catalytic cycle involves the substitution (and the release) of the boronato alkyne by HBPin*, regenerating the actual catalyst of this reaction, Int1, is slightly exergonic and exothermic (ΔG = 6.3 and ΔH = 11.5 kcal · mol⁻¹).

Importantly, we believe that in presence of HBPin, dicaticionic 1 is not regenerated due to rather high ΔG and ΔH required for this step (28.2 and 41.5 kcal · mol⁻¹, respectively). Overall, the dehydrogenative borylation reaction is both exergonic and exothermic with ΔG = −8.7 and ΔH = −10.6 kcal · mol⁻¹.

The proposed mechanism for the hydroboration of terminal alkynes (Scheme 4b) is speculative at this point, thus its DFT calculations are not included here (see ESI, Figure S69 for DFT calculated possible mechanistic picture).

Conclusion

To conclude, we showed here the synthesis of an air-stable dicaticionic Zn²⁺ complex in TPPh ligand (1). At r.t. 2 mol% of 1 selectively catalyze the dehydrogenative borylation of terminal alkynes, while 0.5 mol% of 1 at elevated temperatures (90°C) promotes selective hydroboration of terminal alkynes. The best conditions for hydroboration were first heating (90°C) 1 (0.5 mol%) with HBPin for ~10 min. followed by addition of alkyne and further heating (90°C). The mode of action for both dehydrogenative borylation and hydroboration were proposed based on experimental observations as well as supported by DFT calculation for the dehydroborylation catalysis. In dehydrogenative borylation 1 is probably the precatalyst, while the actual catalyst is Int1 in which the H–BPin bond is activated by 1. In the hydroboration, however, that catalyst is most probably the mixture of boronien-type species ([L · BPin]+) that are formed in the reaction of 1 with excess of HBPin after heating or prolonged reaction time. Remarkably, 1, to the best of our knowledge, is the first single system that can “on demand” selectively promote either dehydrogenative borylation or hydroboration reactions of terminal alkynes, depending on 1’s...
loading and reaction conditions only. We continue to study the chemistry of these fascinating Zn(II) dicatonic systems and their catalytic ability in other hydrodeamination reactions.

Experimental Section

General considerations

All experiments were carried out under an anhydrous N₂ atmosphere using standard Schlenk and glovebox techniques. All glassware was oven dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. Dichloromethane (DCM), toluene and hexane were dried using Vacuum Atmospheres solvent purification system. 1,2-difluorobenzene (α-DFB) and acetonitrile, were dried over CaH₂ and distilled from it. Potassium tetrakis(pentafluorophenyl)borate (KAPPA APEX II diffractometer equipped with an APEX II CCD source (Bruker,2014/5) was added to a dry tetrahydrofuran (15 mL) solution of TPPh (0.31 g, 1.0 mmol) under N₂ -2132153; The crystals were mounted on a cryoloop with HBPin (α-DFB) and acetonitrile, were dried over CaH₂ and distilled from it. Potassium tetrakis(pentafluorophenyl)borate (1.44 g, 2.0 mmol) was added to a dry tetrahydrofuran (15 mL) solution of TPPh (0.31 g, 1.0 mmol) under N₂ -2132154; All the crystal structures were solved through SHELXT[22] and the structures were refined using SHELXL[25] and the structures were refined using SHELXL[25]. All non-hydrogen atoms were refined anisotropically. All the figures were generated using Mercury 3.10.2. CCDC numbers for the X-ray structures: 3J – 2132153; 2 – 2132154; 3a – 2132155.

Synthesis and spectroscopic data

Synthesis of TPPh-ZnCl₂ (2): Zinc chloride (0.28 g, 1.0 mmol) was added to a dry tetrahydrofuran (15 mL) solution of TPPh (0.31 g, 1.0 mmol) under N₂ and magnetic stirring. After 12 h of stirring, tetrahydrofuran was removed under reduced pressure, and 15 mL of dichloromethane were added. 2 was crystallized from a concentrated solution of dichloromethane, (0.40 g, 90%). ¹H NMR (CDCl₃, 400 MHz): δ = 3.09 (s, 6H), 7.33 (d, J = 7.8 Hz, 3H), 7.37 (t, J = 6.5 Hz, 3H), 7.81 (t, J = 7.64 Hz, 3H), 8.93 (b, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 32.5 (d, J = 25.8 Hz), 122.5, 125.6, 139.2, 149.9, 157.0. ¹⁹F NMR (CDCl₃, 162 MHz): δ = –14.2.

Synthesis of [TPPh-Zn][BF₄]₂ (1): Potassium tetrakis(pentafluorophenyl)borate (1.44 g, 2.0 mmol) was added to a dry 1,2-difluorobenzene solution of 2 (0.45 g, 1.0 mmol). The reaction mixture was left to stir overnight at 120°C. The precipitated KCl was removed by filtration and the solvent was evaporated to obtain 1 as white solid (1.5 g, 90%). ¹H NMR (DMSO- d₄, capillary in dichloromethane, 400 MHz): δ = 3.12 (d, J₁₋₂ = 5.2 Hz, 6H), 7.65 (d, J = 7.9 Hz, 3H), 8.34 (t, J = 7.9 Hz, 3H), 8.38 (s, J = 7.9 Hz, 3H), 8.66 (d, J = 5.2 Hz, 3H). ¹³C NMR (DMSO-d₄, capillary in dichloromethane, 100 MHz): δ = 29.0 (d, J = 29 Hz, 3H), 124.9, 127.0, 134.5, 136.3, 136.9, 138.8, 142.9, 145.4, 146.2, 148.6, 151.1. ¹⁹F NMR (DMSO-d₄, capillary in dichloromethane, 162 MHz): δ = –10.9; ¹⁹F NMR (DMSO-d₄, capillary in DCM, 376 MHz): δ = –134.2, –163.9 (J, J = 20.0 Hz), –168.0 (t, J = 17.0 Hz). ¹⁹B NMR (DMSO-d₄, capillary in DCM, 128 MHz): δ = –17.4.

General procedure for dehydrogenative borylation of alkynes with HBPin: To a 1:1.05 solution of alkyne and HBPin in 1,2-difluorobenzene in J-Young tube, 1 (2 mol%) was added and the reaction mixture was stirred for the indicated period of time (see table S1, ESI). The conversion was determined by ¹H and ¹³C NMR spectroscopy. The products of the dehydrogenative borylation were purified by filtration of the reaction mixture through celite column using hexane as eluent. Evaporation of the volatiles under vacuum afforded the corresponding product and further purified by silica gel column chromatography eluted with EtOAc and hexane mixtures.

General procedure for hydroboration of alkynes with HBPin: J-Young tube was charged with 1.2 equivalent HBPin, (0.5 mol%), 1 and 0.3 mL 1,2-difluorobenzene. The mixture was heated for ~10 min at 90°C before addition of 1 equiv. of alkyne and further heated at 90°C for indicated period of time (see table S2, ESI). The conversion was determined by ¹H and ¹³C NMR spectroscopy. The products of hydroboration were purified by filtration of the reaction mixture through celite column using pentane as eluent. Evaporation of the volatiles under vacuum afforded the corresponding product. The product was further purified by silica gel column chromatography eluted with EtOAc and hexane mixture.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: dehydrogenative borylation · FLP · HBpin · hydroboration · zinc

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