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ARTICLE

# Phenalenyl-based Nickel Catalyst for Hydroboration of Olefins under Ambient Conditions

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In this report, nickel-catalyzed hydroboration of vinylarenes and aliphatic alkenes are investigated. The non-innocent phenalenyl ligand moiety in the nickel complex $Ni(PLY)_2(THF)_2$ (**1**) was utilized as an electron reservoir for the selective hydroboration reaction in the presence of pinacolborane under ambient conditions. The mechanistic investigations revealed that alkene hydroboration reaction takes place through a single electron transfer (SET) from the phenalenyl ligand backbone leading to the cleavage of B–H bond.

## Introduction

Transition metal complexes bearing non-innocent ligands have attracted a great deal of interest.[1] These non-innocent ligands are able to act as redox reservoir and can play crucial role in new catalyst design.[2-3] Such a catalytic process can avoid the situation of metals indulging to an unfavourable oxidation states and thus enables conceptually new catalytic mechanism. In this way, redox non-innocent ligands allow the first-row transition metals to mimic the catalytic properties of noble metals.[4-6] The first successful application of homogeneous iron catalysts bearing non-innocent ligands for ethylene polymerization was reported by Brookhart and co-workers in 1998[7] in which a bis(imino)pyridine ligand played an important role in the catalytic cycle by utilizing its electron storage capacity in combination with an iron based pre-catalyst. Later on, Chirik and co-workers developed intramolecular cyclization of dienes and enynes via $[2\pi + 2\pi]$ cycloaddition that benefited from the unique electronic structure of the iron complexes imposed by the presence of a non-innocent ligand.[8-9] The bis(imino)pyridine iron complexes were also successfully applied to olefin hydrogenation and hydrosilylation catalysis.[10-12] Chirik and co-workers also reported the addition of pinacolborane to terminal-, 1,1- and 1,2-disubstituted alkenes with the same catalyst.[13] Recently, Ritter et al. reported the iminopyridine-derived iron complexes as catalysts for the regioselective 1,4-hydroboration of substituted 1,3-dienes.[14]

In this context, herein, we present an odd alternant hydrocarbon phenalenyl (PLY) ligand as the redox non-innocent ligand.[15] The major advantage of this odd alternant hydrocarbon based on phenalenyl moiety is the presence of an energetically accessible empty non bonding molecular orbital (NBMO)[16] in their cationic state, which can be generated on coordination with a metal ion.[17] As a result, acceptance or transfer of electron(s) takes place through this NBMO unlike other non-innocent ligands which normally use their anti-bonding orbital. In fact, the use of the NBMO of phenalenyl can be traced back to their exceptional material properties as organic conductors,[18] organic magnets,[19] electronic switch,[20] soft battery,[21] molecular memory device[22] and cathode material.[23] Recently, its application in catalytic activation of various substrates is gaining increasing attention.[24-29] Very recently, we observed that redox participation of the PLY ligand results in development of an excellent nickel based catalyst to perform regioselective hydrosilylation of a wide variety of olefins.[30] This study encourages us to explore further applications in designing base metal catalysis assisted by phenalenyl backbone. Herein we report regioselective nickel-catalyzed hydroboration of vinylarenes and aliphatic alkenes by using a nickel-phenalenyl $Ni(PLY)_2(THF)_2$ (**1**) complex in the presence of pinacolborane at room temperature.

It may be worth to note that, hydroboration of alkenes is the most convenient method for the synthesis of alkylboron compounds.[31-33] Alkylboranes are versatile intermediates in synthesis of alcohols, amines, and carboxylic acids[34-38] and widely employed for carbon−carbon bond formation in the pharmaceutical industry. Most catalytic alkene hydroborations classically required precious metals, such as Rh[39-42] and Ir.[43-44] However, the low abundance, economic constrains, and environmental issues have encouraged the investigation of earth-abundant inexpensive base–metals as alternatives.[45] While Fe,[46-48] Co,[49-50] Cu[51-52] catalyzed hydroboration of terminal alkenes with pinacolborane (HBpin) has been studied, but the hydroboration of terminal alkenes with nickel catalyst is less-established.[53] Recently, Ye and co-workers reported a base-free hydroboration of alkenes with bis(pinacolato)diboron ($B_2pin_2$) using $Ni(cod)_2/P(t\text{-}Bu)_3$ system at 75 °C.[54] Very recently, Shimada and co-workers developed a Ni-catalyzed hydroboration of olefins with

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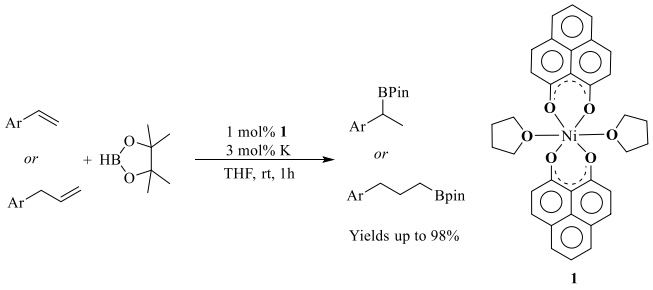
$B_2pin_2$ and water.[55] Herein we report hydroboration reaction catalysed by a Ni catalyst exhibiting both high activity and regioselectivity for allyl and vinylarenes at room temperature (Scheme 1).

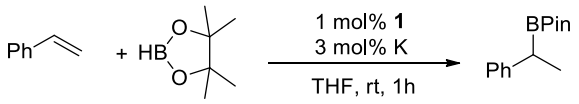



**Scheme 1** Summary of present work.

## Results and discussion

Previous studies from our laboratory have demonstrated that the nickel phenalenyl complex **1** is a highly active catalyst for the hydrosilylation of aliphatic alkenes.[30] Catalytic hydrosilylation proceeded with high selectivity and addition of $Ph_2SiH_2$ to terminal alkenes furnished exclusively terminally silylated products. These results inspired us the exploration of the phenalenyl nickel catalyst **1** for the hydroboration reaction.

**Table 1** Optimization of the catalyst and solvent for the nickel catalyzed hydroboration of styrene[a]

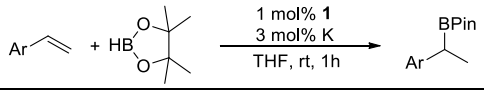


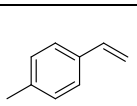
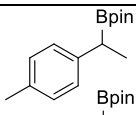
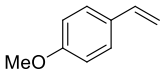
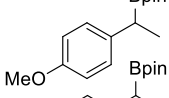
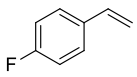
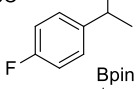
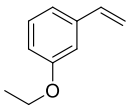
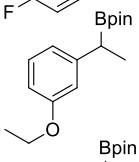
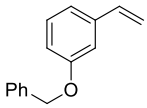
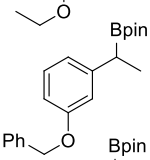
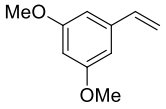
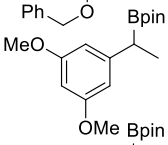
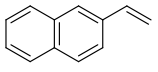
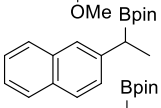
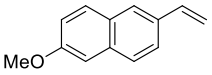
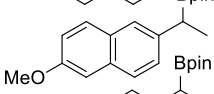
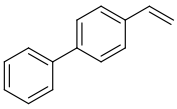
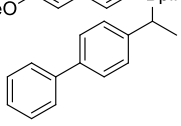

| Entry | Catalyst | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | **1** | THF | 98 |
| 2 | **1** | DMSO | 62 |
| 3 | **1** | $C_6H_6$ | <5 |
| 4[c] | **1** | THF | NR |
| 5 | $NiCl_2$ | THF | <5 |
| 6 | $Ni(acac)_2(MeOH)_2$ | THF | <5 |
| 7 | PLY(O,O) | THF | NR |
| 8[d] | - | THF | NR |

[a] Reaction conditions: HBpin (0.5 mmol) and styrene (0.5 mmol) in THF (1 mL) at 25 °C. [b] The reported yields are $^1$H NMR spectroscopic yields. [c] Without potassium. [d] Without catalyst **1**. NR = No reaction, acac = acteylacetanato.

The initial screening was investigated with the styrene and HBpin in the presence of catalyst **1** and potassium as a reductant in THF at room temperature for 1h (Table 1). To our great delight, a quantitative conversion of Markovnikov hydroboration product was observed (Table 1, entry 1). When the reaction was performed in DMSO as solvent, lesser conversion was obtained (62% Table 1, entry 2), and in benzene, it afforded very low conversion (<5%; Table 1, entry 3). As a control, the hydroboration reaction using catalyst alone (1 mol %) in absence of K gave no product (Table 1, entry 4). The reaction using $NiCl_2$ or $Ni(acac)_2(MeOH)_2$ in the presence of K also gave only trace amount of product (Table 1, entries 5 and 6). Furthermore, to establish that the PLY-based nickel complex is essential for the reaction, we performed catalysis with only PLY ligand and potassium, which did not result in any hydroborylated product (Table 1, entry 7). No hydroboration product was observed without catalyst **1** (Table 1, entry 8). All these results on control experiments clearly established the role of phenalenyl ligand in the catalyst **1**.

**Table 2** Hydroboration of vinylarenes with HBpin catalyzed by **1**.[a]



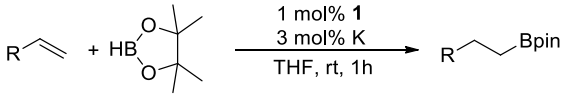

| Entry | Alkene | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 96 |
| 2 |  |  | 94 |
| 3 |  |  | 95 |
| 4 |  |  | 84 |
| 5 |  |  | 83 |
| 6 |  |  | 72 |
| 7 |  |  | 96 |
| 8 |  |  | 92 |
| 9 |  |  | 95 |

[a] Reaction conditions: vinylarene (0.5 mmol), HBPin (1 equiv.), $Ni(PLY)_2(THF)_2$ (1 mol%), K (3 mol%), THF (1 mL), RT. [b] Yields are reported after purification by column chromatography.

With the optimized conditions in hand, we examined hydroboration of various functionalized vinylarenes under optimum reaction conditions using complex **1** (1 mol %) and K (3 mol %) in THF for 1h at room temperature and pinacolborane as the hydroborating reagent (Table 2). In all cases, the regioselectivity was excellent, exclusively Markovnikov alkylboronate product was observed, that

has been proven challenging for iron and rhodium catalysts.[56-57] Vinylarenes with an electrondonating substituent at para-position on the phenyl group gave the alkylboronate product in 96% and 94% isolated yield (Table 2, entries 1-2), respectively. The halogen-substituted vinylarenes were compatible with the reaction conditions, and the desired product was obtained without compromising with the yield and regioselectivity; the reaction of 4-fluorostyrene (Table 2, entry 3) afforded the product in 95% isolated yield. The meta-substituted vinylarenes (Table 2, entries 4 - 5) also reacted with high regioselectivity like para-substituted vinylarenes. The electron donating group at both meta positions of benzene ring did not diminish the yield and regioselectivity. The reaction of 3,5-dimethoxystyrene (Table 2, entry 6) also resulted in the desired product in 72% yield. The reaction of 2-vinylnaphthalene (Table 2, entry 7) resulted in excellent yield (96%).

**Table 3** Hydroboration of various aliphatic alkenes with HBpin catalyzed by **1**.[a]




| Entry | Alkene | Product | Yield (%)[b] |
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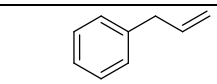
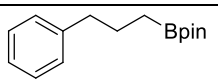
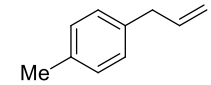
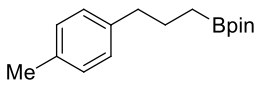
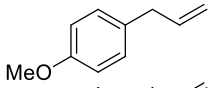
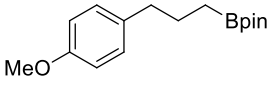
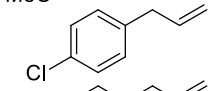
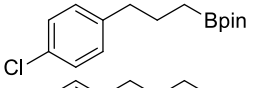
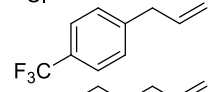
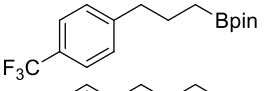
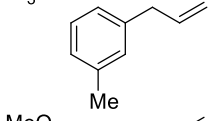
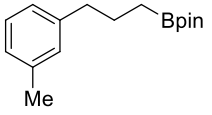
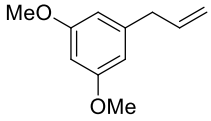
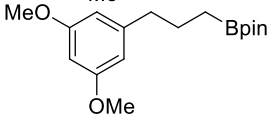
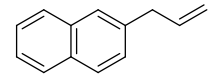
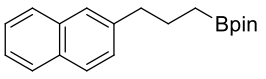
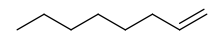
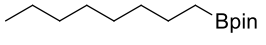
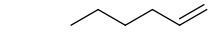
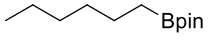
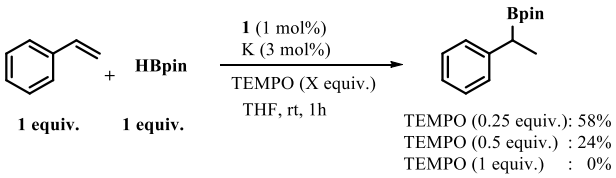
| 1 |  |  | 78 |
| 2 |  |  | 77 |
| 3 |  |  | 76 |
| 4 |  |  | 64 |
| 5 |  |  | 69 |
| 6 |  |  | 62 |
| 7 |  |  | 56 |
| 8 |  |  | 68 |
| 9 |  |  | 72 |
| 10 |  |  | 74 |

[a] Reaction conditions: alkene (0.5 mmol), HBPin (1 equiv.), $Ni(PLY)_2(THF)_2$ (1 mol%), K (3 mol%), THF (1 mL), RT. [b] Yields are reported after purification by column chromatography.

In the case of 6-methoxy-2-vinylnaphthalene (Table 2, entry 8), the hydroborylated product was obtained in 92% yield, which is an intermediate to synthesize nonsteroidal anti-inflammatory drug Naproxen™ ((R)-2-(6-methoxynaphthalen-2-yl)propanoic acid).[58] The reaction of 4-vinylbiphenyl (Table 2, entry 9) resulted the product in excellent yield (95%). It may be noted that the preceding result using a nickel catalyst required 60 °C for 18h while the current method works under ambient conditions.[53]

Next, we examined hydroboration of aliphatic olefins (unactivated alkenes) considering various functionalized alkenes with pinacolborane using **1** as the catalyst (Table 3). When the hydroboration of aliphatic alkenes was performed with the optimized conditions, the anti-Markovnikov hydroboration products were obtained (olefin isomerized product was also detected as a side product by $^1H$ NMR spectroscopy). This divergent regioselectivity of vinylarenes and aliphatic alkenes was also previously observed by using a dinuclear pincer cobalt complex.[59] The catalyst **1** successfully hydroborated the allyl benzene and substrate bearing electron donating substituent such as methyl or methoxy on the phenyl group at para-position yielding the corresponding alkylboronates with 78%, 77% or 76% yield (Table 3, entries 1-3). 4-chloro allylbenzene was tolerated under the reaction conditions giving linear boronic ester in good yield with no cleavage of the aryl-halide bond (Table 3, entry 4). The olefin bearing trifluoromethyl group at *para* position can also be hydroborated using pinacolborane with satisfactory yield 69% (Table 3, entry 5). Good yields were observed for allyl benzene bearing electron-donating groups at *meta* position (Table 3, entries 6-7). The reaction of 2-allylnaphthalene (Table 3, entry 8) resulted in 68% yield. Non-functional linear terminal alkenes such as 1-hexene and 1-octene were selectively hydroborated and the corresponding alkylboronate esters were isolated with 72-74% yields (Table 3, entries 9 -10).

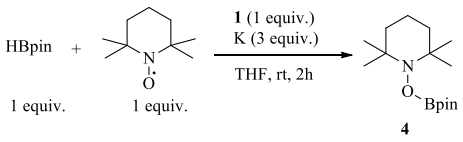
Based on our earlier report,[30] we anticipated that the olefin hydroboration may follow a radical pathway. To check this assertion further, a radical scavenger TEMPO was added (two runs with 0.25 and 0.5 equiv.) to the reaction mixture which drastically reduced the yield of the hydroborylated product to 58% and 24%, respectively and no hydroborylated product was observed with 1 equiv. of TEMPO (Scheme 2)




**Scheme 2** Reaction inhibition in the presence of TEMPO.

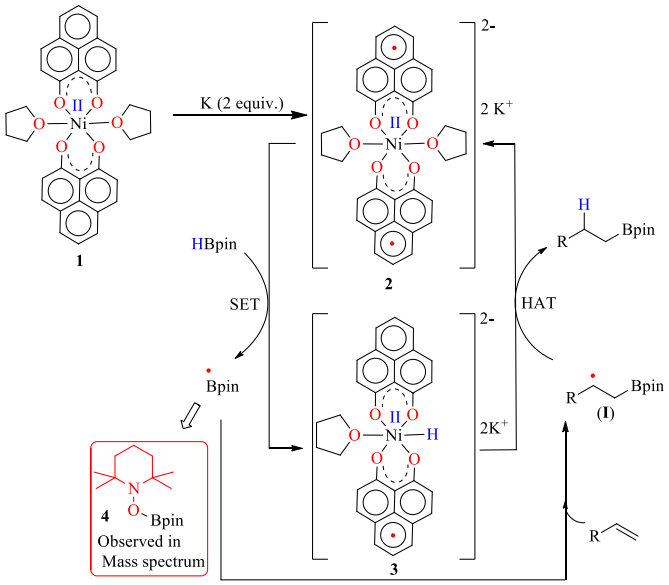
Based on these preliminary data and our understanding on mechanism of nickel-catalyzed alkene hydrosilylation processes,[29] we propose the mechanism of nickel-catalyzed alkene hydroborations involving a radical pathway. The two electron reduction of **1** with potassium metal gives a biradical nickel complex **2**. A single electron transfer (SET) occurs from **2** to HBpin to

generate a boryl radical which subsequently adds to the olefin resulting in the formation of a borylated alkyl radical (**I**). The generation of boryl radical during this hydroboration has been unambiguously authenticated by trapping the TEMPO-adduct of the putative radical **4** and characterized by mass spectrometry (Scheme 3).




**Scheme 3** Reaction of trapping boryl radical in the presence of TEMPO.

Upon SET, **2** transforms into an anionic monoradical species comprising nickel hydride, **3** (Scheme 4). Multiple attempts to capture such Ni-H species failed and we do not fully discard the possibility of a hydride transfer from B-H bond to phenalenyl backbone. The boryl radical subsequently adds to the olefin resulting in the formation of a borylated alkyl radical (**I**). Upon subsequent hydrogen atom transfer (HAT), the borylated alkyl radical transforms into the hydroborylated product and regenerates the active catalyst **2.**




**Scheme 4** A plausible mechanism for catalytic hydroboration of olefin by **1** through PLY based radical initiation.

## Conclusions

In conclusion, we have shown that [Ni(PLY)$_2$(THF)$_2$] complex can be an effective catalyst for hydroboration of alkenes using pinacolborane at room temperature. Notably, the catalyst is equally active for the hydroboration of vinylarenes and aliphatic alkenes with high selectivity of boronate esters. The generation of phenalenyl ligand centered radicals upon reduction of **1** plays a key role during this hydroboration reaction.

## Experimental

**General methods and instrumentation.** All manipulations were performed under a dry and oxygen free atmosphere (argon) using standard Schlenk line techniques or inside a glovebox maintained below 0.1 ppm of $O_2$ and $H_2O$ levels, utilizing oven-dried (130 $^oC$) glassware after evacuation while hot prior to use. All solvents were distilled from Na/benzophenone prior to use. All other chemicals were purchased from Sigma–Aldrich and used as received. The HRMS data were obtained using a Finnigan MAT 8230 instrument. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). $^1$H, $^{13}$C and $^{11}$B NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. All chemical shifts were reported in ppm using tetra methyl silane as a reference. Chemical shifts ($\delta$) downfield from the reference standard were assigned positive values. Ni(PLY)$_2$(THF)$_2$ (**1**) was prepared according to the literature procedure.[30]

**General procedure for the hydroboration of vinylarenes with catalyst 1.** To a stirred solution of Ni(PLY)$_2$(THF)$_2$ (3 mg. 0.005 mmol) and K (0.6 mg, 0.015 mmol) in THF (1 mL), the pinacolborane (0.5 mmol) and vinylarene (0.5 mmol) were added at room temperature. The solution was stirred at room temperature for 1 h, and the progress of the reaction was monitored by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. The $^1$H NMR spectroscopic analysis of the resulting solution revealed the formation of product. The solution was concentrated under vacuum, and the residue was purified by column chromatography using hexane as an eluent. The final product was characterized by $^1$H, $^{13}$C and $^{11}$B NMR spectroscopy.

**General procedure for the hydroboration of aliphatic alkenes with catalyst 1.** To a stirred solution of Ni(PLY)$_2$(THF)$_2$ (3 mg. 0.005 mmol) and K (0.6 mg, 0.015 mmol) in THF (1 mL), the pinacolborane (0.5 mmol) and aliphatic alkene (0.5 mmol) were added at room temperature. The solution was stirred at room temperature for 1 h, and the progress of the reaction was monitored by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. The $^1$H NMR spectroscopic analysis of the resulting solution revealed the formation of product. The solution was concentrated under vacuum, and the residue was purified by column chromatography using hexane as an eluent. The final product was characterized by $^1$H, $^{13}$C and $^{11}$B NMR spectroscopy.

**Procedure for reaction inhibition in presence of radical scavenger TEMPO.** Ni(PLY)$_2$(THF)$_2$ (0.005 mmol) and K (0.015 mmol) in THF (1 mL) were taken and HBpin (0.5 mmol), styrene (0.5 mmol) and TEMPO (0.25/0.5/1 mmol) were added to it at room temperature. The reaction was stirred at room temperature for 1 h and then quenched by exposing the reaction mixture to air. The

solution was concentrated under vacuum and the product was purified by column chromatography using hexane as an eluent.

**Procedure for trapping of pinacolboryl radical (4).** $Ni(PLY)_2(THF)_2$ (0.5 mmol) and K (1.5 mmol) in THF (1 mL) were taken and HBpin (0.5 mmol) and TEMPO (0.5 mmol) were added to it at room temperature. The reaction was stirred at room temperature for 2 h and then the reaction mixture was subjected to HRMS characterization in acetonitrile solvent.

## Conflicts of interest

There are no conflicts to declare

## Acknowledgements

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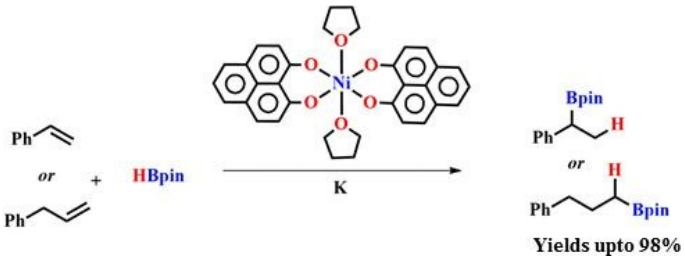


Catalytic hydroboration of alkenes are reported using the redox active phenalenyl ligand assisted nickel complex $Ni(PLY)_2(THF)_2$ in the presence of pinacolborane under ambient conditions.