Hydroboration and reductive amination of ketones and aldehydes with HBpin by a bench stable Pd(II)-catalyst

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A palladium (II) complex [(κ[4]-{1,2-C_6H_4(N=CH-C_6H_4O)$_2$}Pd] (**1**) supported by a dianionic salen ligand [1,2-C_6H_4(N=CH-C_6H_4O)$_2$][2-] (**L**) was synthesised used as a molecular pre-catalyst in the hydroboration of aldehydes and ketones. The molecular structure of Pd(II) complex **1** was established by single-crystal X-ray diffraction analysis. Complex **1** was tested as a competent pre-catalyst in the hydroboration of aldehydes and ketones with pinacolborane (HBpin) to produce corresponding boronate esters in excellent yields at ambient temperature under solvent-free conditions. Further, the complex **1** proved to be a competent catalyst in the reductive amination of aldehydes with HBpin and primary amines under mild and solvent-free conditions to afford a high yield (up to 97%) of corresponding secondary amines. Both protocols provided high conversion, superior selectivity and broad substrate scope, from electron-withdrawing to electron-donating and heterocyclic substitutions. A computational study based on density functional theory (DFT) revealed a reaction mechanism for Pd-catalysed hydroboration of carbonyl species in the presence of HBpin. The protocols also uncovered the dual role of HBpin in achieving the hydroboration reaction.

Introduction

Organoborane reagents are essential ingredients in numerous synthetic processes due to their acute reactivity and are thus widely used. As synthetic intermediates, they have been instrumental in the introduction of various functional groups and carbon–carbon bond-forming processes over several years. Suzuki-Miyaura coupling and Petasis borono–Mannich reactions are considered well-known examples of such applications.[1-2] Hydroboration of unsaturated organic compounds such as alkenes, alkynes, nitriles, amides, and carbonyls is used as the most straightforward approach to produce an organoboron compound.[3] The selective and efficient reduction of carbonyl compounds to corresponding alcohols has emerged as a significant transformation in modern science.[4] Traditional methods for the reduction of carbonyl compounds require stoichiometric agents, such as $NaBH_4$ or $LiAlH_4$, and H_2, to be used under high pressure, and have limitations such as poor functional group tolerance, production of a large amount of waste, laborious isolation, several purification steps and safety issues.[5-7]

Nowadays, metal-catalysed hydrogenation of carbonyl compounds has been widely employed for the reduction of carbonyl compounds, although it demands the use of flammable hydrogen gas and harsh reaction conditions.[8] In view of these limitations associated with the reduction of carbonyl compounds, metal-catalysed hydroboration has emerged as an excellent alternate approach in organic transformations, as organoborates are stable towards air and moisture, as well as being non-toxic.[9] To date, there are reports of a wide variety of metal catalysts from main group elements, including catalysts based on alkali or alkaline earth metals, namely, Al,[10] Si,[11]

Ge[12] and Sn,[13] as well as rare earth metal catalysts such as those based on La[14] and Yb,[15] which have been used in the hydroboration of carbonyl compounds. Transition metals such as Ti,[16] Mn,[17] Fe,[18] Mo,[19] Rh,[20] Ru,[21] Co[22] and Cu[23] have also been used as bases for developing catalysts. Recently, we introduced a zinc complex as a competent catalyst in the chemoselective hydroboration of carbonyl compounds.[24] There are a few examples of organocatalysed hydroboration of carbonyl compounds also in literature.[25] However, there are only a few reports on metal- and solvent-free hydroboration reactions of aldehydes and ketones, since they require an excessive amount of HBpin and high temperatures.[26] Further, recent reports reveal that the formation of organoboron compounds from aldehydes and ketones proceeds via hidden boron catalysts derived from HBpin, HBcat or 9-BBN.[27] Surprisingly, there are reports of one or two examples of palladium-catalysed hydroboration of carbonyl compounds in published scientific literature.[28] Recently, Huang and co-workers reported the palladium-catalysed regioselective hydroboration of aryl alkenes using B_2pin_2.[29] Additionally, palladium-promoted hydroboration can be seen only with respect to CO_2, alkene and alkyne functionalities.[30] Furthermore, very recently, Sarkar et al. studied the selective reduction of carbonyl compounds in $CDCl_3$ employing a guanidine-based palladium complex.[31]

In contrast, reductive amination is considered an entrenched protocol for the efficient and selective synthesis of unsymmetrically substituted amines.[32] This method has garnered considerable attention in chemical synthesis since it is environmentally benign.[33] Despite the use of harsh reaction conditions, as evident from the preparation of various primary amines from the coupling of carbonyl and amines, metal-catalysed reductive amination reactions demonstrate a new avenue for organic transformations.[34] Typically,

metal-catalysed processes are considered a promising synthetic route for defunctionalisation reactions.

In this context, we report here the synthesis and solid-state structure of a palladium(II) complex supported by the dianionic salen ligand [1,2-C$_6$H$_4$(N=CH-C$_6$H$_4$O)$_2$]$^{2-}$ (**L**) and the catalytic efficiency of Pd(II) metal complex (**1**) in the hydroboration of a wide variety of aldehydes and ketones in the presence of pinacolborane (HBpin). In addition, we report the catalytic reductive amination of carbonyl compounds with HBpin and primary amines using Pd(II) complex **1** under mild and solvent-free conditions to afford high yields of the corresponding N-boryl amines. A computational study was also performed to gain mechanistic insight into the hydroboration reaction.

Results and Discussion

*Synthesis and formulation of the Schiff base (**H₂L**) and palladium(II) complex (**1**).*

The palladium (II) complex [(κ^4-{1,2-C$_6$H$_4$(N=CH-C$_6$H$_4$O)$_2$}Pd] (**1**) was synthesised in excellent yield by the addition of PdCl$_2$(PPh$_3$)$_2$ to the protio ligand **H2L** in a 1:1 molar ratio in a 4:1 medium of MeOH-CHCl$_3$ in the presence of a catalytic amount of Et$_3$N (Scheme 1). Complex **1** was characterised using standard spectroscopic and analytical techniques. The solid-state structure of Pd complex **1** was confirmed by single-crystal X-ray diffraction analysis.

The resonance signal of the imine proton in the ^{1}H NMR spectra of complex **1** was observed at δ_H = 8.56 ppm, which is in the same range as that of the protio ligand [**H₂L**]. Single crystals of complex **1** suitable for X-ray analysis were grown from the MeOH-CHCl$_3$ (4:1) mixture through slow evaporation at room temperature.

Scheme 1. Synthetic routes for the Schiff base and palladium complex **1** formulation.

The molecular structure of complex **1** in the solid state reveals that the mononuclear Pd(II) complex **1** crystallises in the $P2_12_12_1$ space group of the orthorhombic system. The pertinent structural refinement parameters are set out in Table TS1. The solid-state structure of complex **1** is given in Figure 1. Dianionic ligand **L** behaves as a tetradentate chelator towards the palladium centre through two nitrogen (N1, N2) and two oxygen atoms (O1, O2) to adopt a near-perfect square planar coordination geometry around the metal ion. The Pd–O bond distances are slightly longer than those of Pd–N distances. During chelation of the ligand with the Pd(II) centre, it was observed that two six-membered chelate rings by N,O-coordination and one five-membered chelate ring by N, N-coordination are formed, which provides more stability to the Pd(II)-salen complex.

The N–Pd–O bond angles are higher than 90^0 while the N–Pd–N bond angles are lower than 90^0. This slight distortion around the Pd(II) centre in the square plane is principally induced by the steric factors of the ligand. In searching for structurally similar Pd(II)-salen complexes, Ping et al. reported a distorted square planar Pd(II) complex containing the N, N'-bis(3,5-di-tert-butylsalicylidene)-1,2-phenylene-diamine ligand and studied the Suzuki-Miyaura reaction. The bond distance and bond angle values of the Pd(II) complex synthesised in our study are higher than those of the Pd(II) complex reported by He and co-workers.[35]
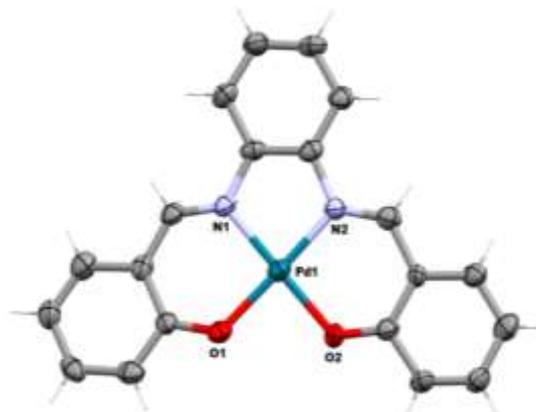

Figure 1. Molecular structure of Pd(II) metal complex **1** in the solid state. Selected bond lengths (Å) and bond angles (°) are given. Pd1–N1 1.968(7), Pd1–N2 1.949(10), Pd1–O1 1.993(8), Pd1–O2 1.979(7), N1–Pd1–N2 84.7(4), N1–Pd1-O1 93.7(4), N1–Pd1-O2 178.4(4), N2–Pd1–O1 178.3(3), O1–Pd1–O2 87.1(3). CCDC No. 2116643.

*Solution property of the Schiff base and palladium(II) complex (**1**).*

The electronic transitions for the Schiff base and its Pd(II) complex (**1**) were recorded in an acetonitrile medium (MeCN) from 200 to 900 nm at room temperature. The Schiff base, **H₂L**, displayed electronic transitions at 234 nm, 269 nm and 330 nm, and the Pd(II) complex exhibited electronic bands at 250 nm, 316 nm, 356 nm and 482 nm. The electronic spectra are displayed in Fig. S5 in ESI. Electronic bands at 230 nm, 270 nm and 346 nm in the UV region for the Schiff base are attributed to π→π* and n→π* electronic transitions.[36] The appearance of electronic bands at 250 nm and 316 nm in the Pd(II) complex presumably correspond to the π→π* and n→π* electronic transitions of ligand origin, while the optical bands at 356 nm and 482 nm may be assigned as phenoxo to Pd(II) electronic transition.[37] The solution phase stability of the Pd(II) complex was examined over five days in an acetonitrile medium under similar experimental conditions. It was observed that the lower energy bands of the Pd(II) complex remain unaffected in solution during this period, which assured us of the solution stability of the Pd(II) complex.

Hydroboration of carbonyl compounds.

A primary analysis of catalytic hydroboration of benzophenone with HBpin was carried out to examine the efficiency of the palladium compound as a pre-catalyst using 1 mol% of catalyst at room temperature. The results are set out in Table 1.

Table 1. Optimisation of Pd(II) complex **1**–catalysed hydroboration of ketones.[a,b]
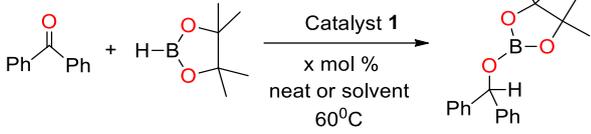
Entry	Catalyst	Catalyst loading (mol%)	Tem (⁰C)	Sol	Time (h)	Isolated Yield[b] (%)
1	None	-	90	Neat	24	30
2	1	1	RT	Neat	26	40
3	**1**	**1**	**60**	**Neat**	**12**	**99**
4	1	0.5	60	Neat	12	50
5	1	1	60	Tol	12	96
6	1	1	60	THF	12	94
7	PdCl$_2$	1	60	Neat	12	74

[a]Reaction condition: Pre-catalyst **1** (1 or 0.5 mol %), HBpin (1 mmol) followed by benzophenone (1 mmol) at specified conditions. [b]Yields were calculated based on ^{1}H NMR integration of characteristic product peak using 20 mol% of 1,3,5-trimethoxybenzene as an internal standard.

To our delight, we observed that the reaction yielded 40% of the corresponding boronate ester after 26 hours when 1 mol% of pre-catalyst **1** was loaded at room temperature (entry 2, Table 1). The product was isolated and was confirmed by ^{1}H and ^{11}B NMR spectral analysis. The yield increased to 99% when the reaction temperature was increased to 60 °C for 12 hours under solvent-free conditions (Table 1 entry 3). It may be noted that only 30% of the product was formed from the reaction mixture in the absence of a catalyst even at 90 °C for 24 hours (Table 1, entry 1). A significantly decreased yield (60%) of the product was observed after 12 hours at 60 °C when 0.5 mol% of pre-catalyst **1** was used (Table 1, entry 4). The use of THF and toluene as the reaction medium did not affect the yield under optimal conditions (Table 1, entries 5–6). A lower yield of the desired product was obtained when a palladium salt such as PdCl$_2$ was used as the pre-catalyst (Table 1, entries 7). Since solvent-free conditions are advantageous and heating the reaction mixture provided a uniform homogenous melt with excellent yield, we identified 60 °C and neat conditions as optimal. With this, we set out to examine the scope of substrates of various carbonyl compounds in the presence of 1 mol% of Pd complex **1**. The generality of the reaction was explored with diverse aromatic, cyclic and heterocyclic ketones, and aldehydes, and the results of the catalytic condensation are presented in Table 2.

Table 2. Substrate scope of Pd(II) complex **1**–catalysed hydroboration of ketones.
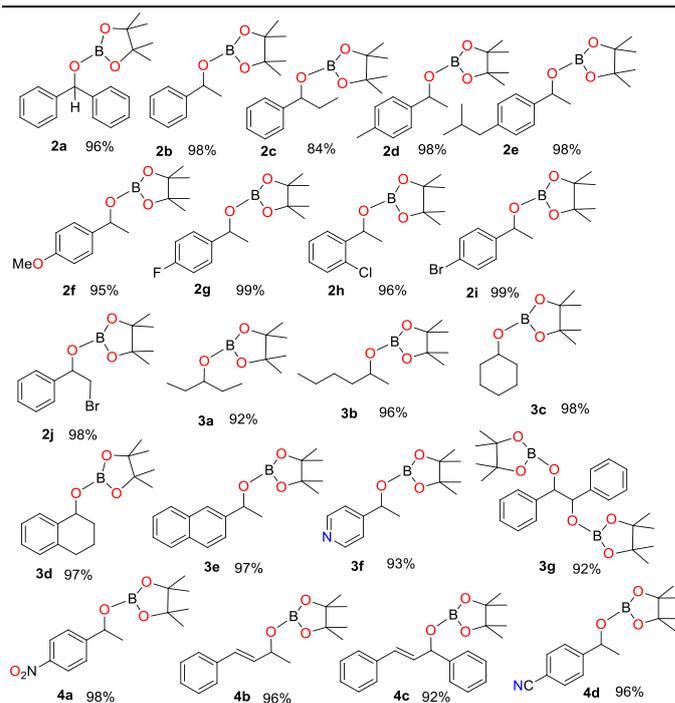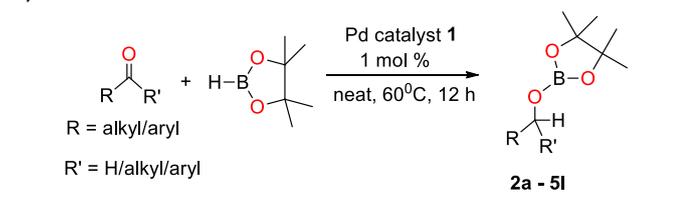
[a]Reaction condition: Pre-catalyst **1** (1 mol %), HBpin (1 mmol) followed by ketones (1 mmol) at 60 °C for 12 hours under neat conditions. [b]Yields were calculated based on ^{1}H NMR integration of characteristic product peak using 20 mol% of 1,3,5-trimethoxybenzene as an internal standard.

The hydroboration of acetophenone proceeded rapidly and a nearly quantitative yield of complex **2b** was obtained within 12 hours at 60 °C (Table 2, entry 2). However, propiophenone furnished a yield of 84% under optimal conditions (Table 2, entry 3). Aryl ketones with electron-releasing groups, such as 4-methyl acetophenone, 4-isobutylacetophenone and 4-methoxy-acetophenone, reacted smoothly with HBpin to form corresponding boronate esters [ArCH(CH$_3$)O(Bpin)] in near-quantitative yields under optimal conditions (Table 2, entries **2d**–**2f**). Similarly, ketone substrates with electron-withdrawing functional groups (such as 4-fluoroacetophenone, 2-chloroacetophenone and 4-bromoacetophenone) were smoothly converted to corresponding boronate esters [ArCH(CH$_3$)O(Bpin)] in excellent yields upon reacting with HBpin at 60 °C under neat conditions (Table 2, entries **2g**–**2i**). 2-bromoacetophenone was quantitatively converted to product **2j** within 12 hours (Table 2, entry **2j**). Further, aliphatic ketones such as 3-pentanone and 2-hexanone, as well as cyclic ketones such as cyclohexanone and tetralone also yielded corresponding boronate esters in the presence of Pd(II) catalyst **1** under optimal conditions (Table 2, entries **3a**–**3d**). Challenging substrates such as 2-acetylnaphthalene and 4-acetylpyridine reacted with HBpin to provide the desired boronate esters in excellent yields (Table 2, entries **3e**–**3f**). Diketones such as benzil reacted smoothly with two equivalents of HBpin in the optimal condition to afford complex **3g** with a yield of 92%, indicating the high catalytic efficiency of Pd complex **1** (Table 2, entry **3g**). Further, to investigate

chemoselectivity of the Pd-catalysed hydroboration reaction, substrates such as 4-nitro acetophenone, benzylideneacetone, chalcone and 4-acetylbenzonitrile were tested with HBpin under optimal conditions (Table 2, entries **4a–4d**). Pd catalyst **1** chemoselectively reduced the carbonyl functional group exclusively to afford a yield of 92–98% (Table 2, entries **4a–4d**).

Table 3. Substrate scope of Pd compound–catalysed hydroboration of aldehydes.[a,b]
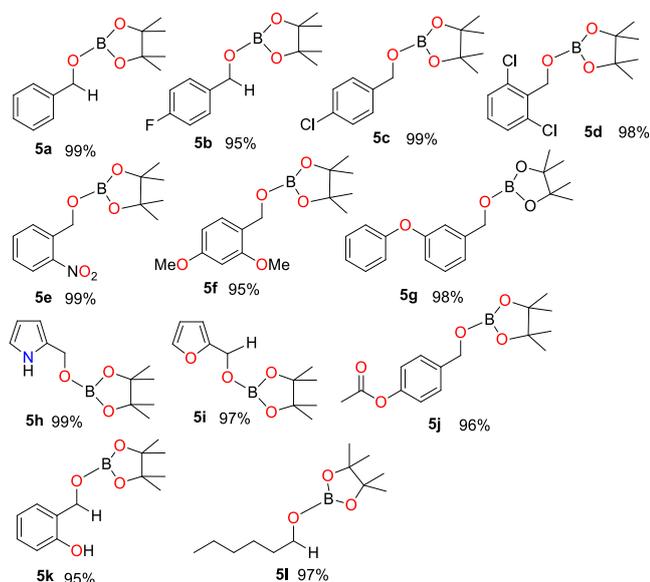
[a]Reaction condition: Pre-catalyst **1** (1 mol %), HBpin (1 mmol) followed by aldehydes (1 mmol) at room temperature for 12 hours under neat conditions. [b]Yields were calculated based on ¹H NMR integration of characteristic product peak using 20 mol% of 1,3,5-trimethoxybenzene as an internal standard.

Aldehydes are another class of substrates which we were keen to utilise in determining the catalytic performance of Pd catalyst **1** in the hydroboration reaction. The hydroboration reaction was tested using one equivalent of benzaldehyde and one equivalent of HBpin at room temperature in the presence of pre-catalyst **1** (1 mol%) under neat conditions. A quantitative yield of product **5a** was obtained within 12 hours (Table 3, entry **5a**). Further, a range of aryl as well as heterocyclic aldehydes with electron-withdrawing and electron-releasing groups were reacted with HBpin for hydroboration reactions at room temperature. The reaction of substituted fluoro-, chloro-, dichloro- and nitro-benzaldehyde and HBpin smoothly furnished a near-quantitative yield of the corresponding boronate (Table 3, entries **5b–5e**). Additionally, the reaction between HBpin and 2,4-dimethoxybenzaldehyde afforded a quantitative yield within 12 hours of reaction time (Table 3, entries **5f**). 3-phenoxybenzaldehyde and heterocyclic aldehydes such as pyrrole-2-carboxaldehyde and furan-2-carboxaldehyde were also quantitatively converted to desired products under optimal conditions (Table 3, entries **5g–5i**). Products **5j** (96% yield) and **5k** (95% yield) with good functional group tolerance were achieved when 4-formylphenylacetate and salicylaldehyde were reacted with

HBpin in the presence of Pd catalyst **1** (Table 3, entries **5j–5k**). The reaction of aliphatic aldehyde such as hexanal and HBpin smoothly furnished a near-quantitative yield of the corresponding boronate (Table 3, entry 5l).

Reductive amination of aldehydes with primary amines.

Reductive amination, a one-pot reaction between aldehydes or ketones and amines in the presence of a reducing agent, is a powerful tool to access biologically and pharmaceutically active molecules.[38] We were interested in exploring the one-pot reductive amination of an aldehyde with primary amines in the presence of Pd(II) catalyst **1** using HBpin as a reducing agent (Scheme 3).
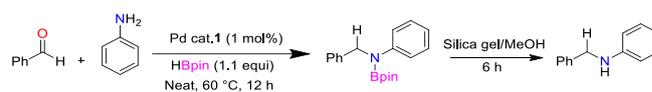

Scheme 3. Reductive amination of benzaldehyde with aniline using Pd(II) complex **1** as a catalyst.

Aldehydes and primary amines with various substituents were subjected to one-pot reductive amination in the presence of Pd catalyst **1** (1 mol% catalyst loading) under neat conditions. Excellent yields of secondary amines were obtained within 12 hours of reaction time and the results are given in Table 4.

The reaction of aniline with benzaldehyde proceeds smoothly to afford the N-benzylamine product with a yield of 90% (Table 4, **6a**). Activated aldehyde, such as 4-methoxy benzaldehyde, reacts with both aniline and electron-rich aniline (such as 4-methoxy aniline) to produce corresponding N-benzylamine products in excellent yields (Table 4, **6b** and **6c**). Deactivated aldehydes with electron-withdrawing groups in the aryl ring, such as 4-chloro-benzaldehyde, 4-bromobenzaldehyde, 2-nitrobenzaldehyde and 4-phenoxy benzaldehyde, react with aniline without any difficulty to form the corresponding N-benzylamine products in high (87–89%) yields (Table 4, **6d–6f, 6i**). The reaction of 2-nitroaniline with benzaldehyde under optimal conditionsafforded N-benzyl-2-nitroaniline (**6k**) in 94% yield.

Table 4. Substrate scope of Pd(II) complex **1**–catalysed reductive amination of aldehydes with primary amines.[a,b]

6a 90% **6b** 86% **6c** 84%

6d 87% **6e** 89% **6f** 88%

**6g** 86% **6h** 88% **6i** 85%

6j 84% **6k** 94%
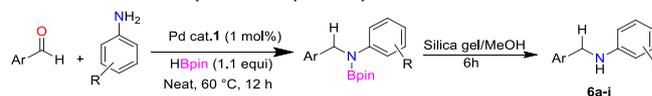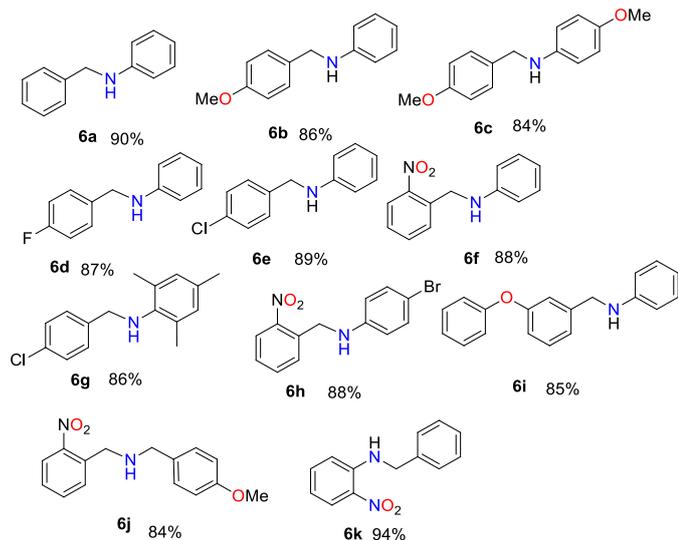
[a]Reaction condition: catalyst **1** (1 mol%), aldehyde (1 mmol), arylamine (1 mmol), and HBpin (1.1 mmol) in neat condition at 60 °C. [b]isolated yield.

A high yield (86%) of product **6g** was achieved from the reaction between 4-chloro-benzaldehyde and 2,4,6-trimethylbenzaldehyde (Table 4, **6g**). The reaction of two electron-deficient substrates, 2-nitrobenzaldehyde and 4-bromo-aniline, afforded a very good yield of N-benzylamine at 60 °C (Table 4, **6h**). The reaction of benzylamine with 4-nitrobenzaldehyde also produced the expected product (**6j**), giving a yield of 84%.

*Computational study of Pd-catalysed hydroboration of carbonyl compounds.*

To understand the reaction mechanism of Pd-catalysed hydroboration of carbonyl compounds, we chose an experimental reaction as depicted in Figure 2 for our computational investigation. We employed the density functional theory (DFT) method (BP86[39,40]-D3[41]/def2-TZVP[42]//BP86-D3/def2-SVP[42] level) to study this reaction and obtain mechanistic insights (Figure 3s and 4).
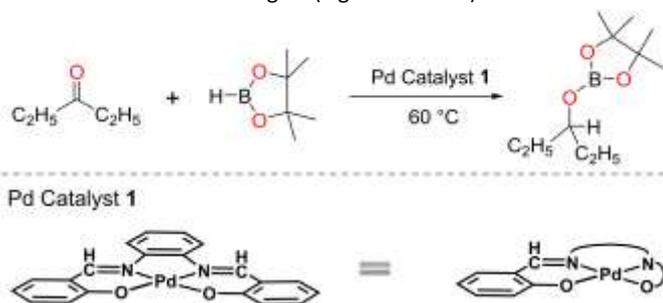

Figure 2. *Top*: Hydroboration reaction of a diethyl ketone compound using Pd catalyst (**1**). Bottom: Pd catalyst **1** (left) and a smaller drawing of **1** to enhance its visual clarity in reaction mechanisms steps.

Reaction progress is discussed in two major sequences: first, the transfer of a hydride from HBpin to catalyst **1**, generating a Pd(II)-hydride complex (**C**) (Figure 3), and second, the use of **C** to reduce a carbonyl species ketone. Two schemes are presented to depict the later sequence (in red and green, Figure 4).

Generation of Pd-hydride complex: Catalyst **1** and HBpin are added to from an adduct **B**, which undergoes via a transition state **TS$_{BC}$** to initiate a hydride transfer from HBpin to Pd with the concomitant formation of a σ B(HBpin)–O$_L$(**1**) bond. **TS$_{BC}$** depletes 32.6 kcal mol^{-1} of energy to yield the Pd(II)-hydride complex (**C**). It is evident that the **1→B→C** conversion is reversible as **C** is least stable in this sequence. The next step, after formation of **C**, is the addition of a ketone followed by hydride transfer from the Pd-centre to the carbonyl carbon. Two schemes are discussed from **C**.
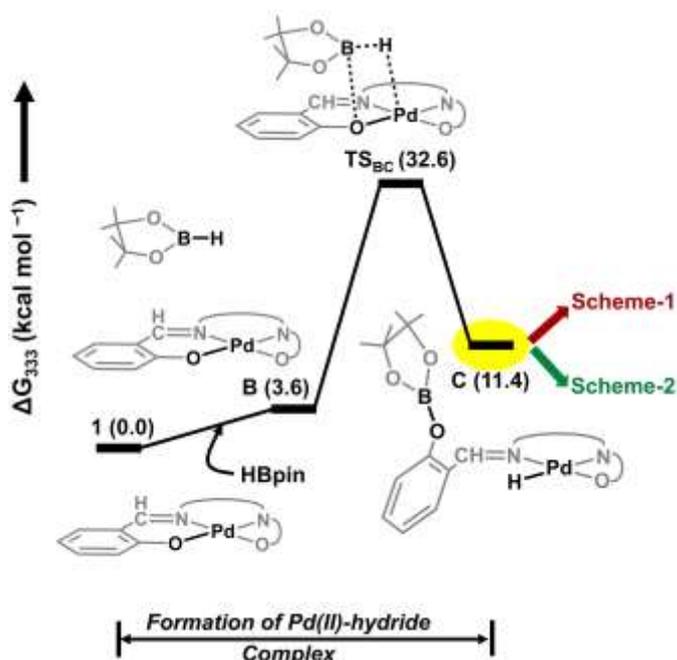
Figure 3. Computational study for the formation of Pd(II)-hydride complex in presence of HBpin. DFT method implemented in the investigation is BP86-D3/def2-TZVP//BP86-D3/def2-SVP. Gibbs free energies ΔG$_{333}$ [kcal mol^{-1}] are relative to **1**.
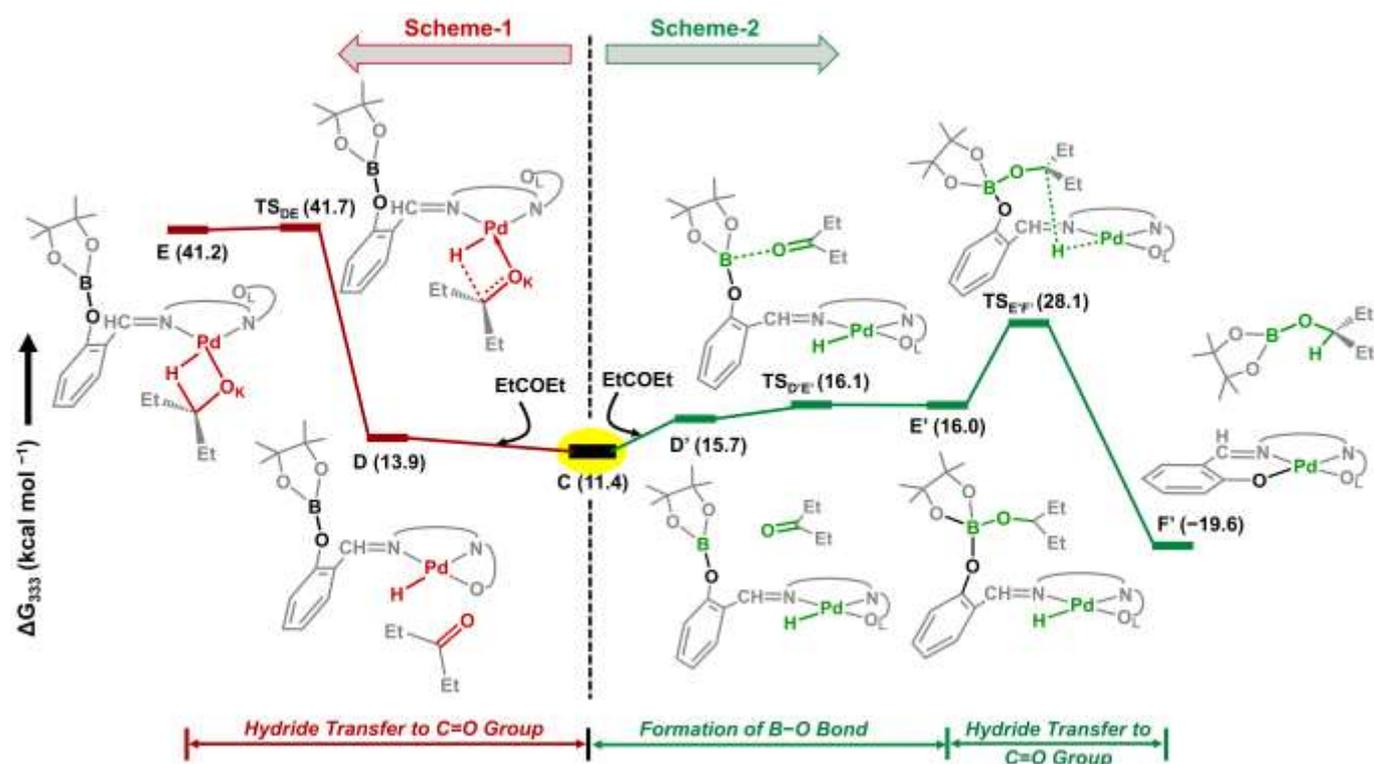
Figure 4. Computational study of Pd-catalysed hydride transfer to a carbonyl compound depicted in Scheme-1 (the left profile) and Scheme-2 (the right profile). DFT method implemented in the investigation is BP86-D3/def2-TZVP//BP86-D3/def2-SVP. Gibbs free energies ΔG_{333} [kcal mol^{-1}] are relative to **1**.

Scheme-1: This scheme begins from adduct **D** in which ketone is placed below the Pd-hydride complex **C**. **D** goes through hydride transfer from Pd to the electrophilic carbonyl carbon via a transition state **TS_DE** with an overall energy barrier of 41.7 kcal mol^{-1}. **TS_DE** results in an unstable intermediate **E**, which features the gain of a Pd–O$_K$ bond but the loss of a Pd–O$_L$ bond. The O$_L$ of the unbound ligand is not coordinated to any site, thus leading to an unstable intermediate **E**. In brief, since Scheme-1 contains energetically demanding transition state, there is a need for an alternate pathway to facilitate the reaction more easily.

Scheme-2: This scheme begins from **D'** where the ketone is above **C**. In term of energy, **D** and **D'** do not differ much. However, in **D'**, the electron-rich oxygen (O$_K$) of the ketone lies in close proximity to the electron-deficient boron site. This placement of complimentary atoms favours the interaction between B(HBpin) and O(ketone) to yield an intermediate **E'**. Subsequently, the transfer of a hydride takes place from Pd to the carbonyl carbon via **TS_E'F'** to yield a stable intermediate **F'** and the Pd catalyst (**1**). In this scheme, the ligand's binding to Pd is intact (Pd–O$_L$ bond), and thus a stable **F'** intermediate is found.

The overall energy barrier for the hydride transfer in Scheme-1 is 47.3 kcal mol^{-1} whereas it is only 28.1 kcal mol^{-1} in Scheme-2. Hence, Scheme-2 is more favourable than Scheme-1. This energy difference can be attributed to the loss of ligand coordination to Pd in Scheme-1. Furthermore, the initial step **1→→C** requires 32.6 kcal mol^{-1}, making **TS_BC** the rate-limiting step in the Pd-catalysed hydroboration of carbonyl compounds.

Dual role of HBpin: In step **1→→C**, HBpin acts as a hydride donor to the Pd catalyst, whereas in step **D'→→F'**, HBpin performs the role of a ketone receiver to provide bonding to carbonyl oxygen (O$_K$). Both these roles of HBpin are important in accomplishing the hydroboration reaction (Figure 5).
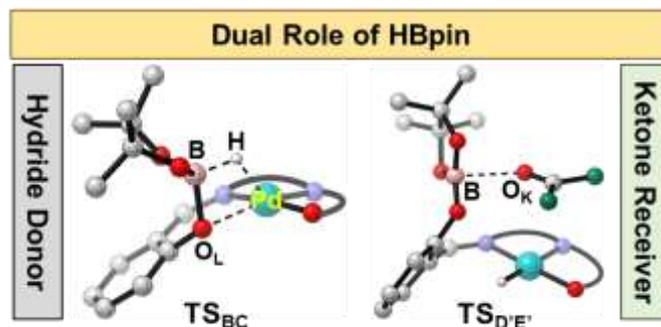
Figure 5. Depicting the dual role of HBpin in Pd-catalysed hydroboration of carbonyl compounds.

Conclusions

In summary, we synthesised and structurally characterised a palladium (II) complex (**1**) supported by a tetra-coordinated dianionic salen ligand. Complex **1** is shown to be a competent pre-catalyst in the hydroboration of aldehydes and ketones with HBpin to afford corresponding boronate esters at ambient temperature under neat conditions with a broad substrate scope. Further, Pd complex **1** was utilised as an efficient catalyst

in the reductive amination of carbonyl compounds with HBpin and primary amines under mild and neat conditions to afford high (up to 97%) yields of secondary amines with wide-ranging substrate scope. The DFT-derived reaction mechanism for Pd-catalysed hydroboration of carbonyl compounds in the presence of HBpin shows that the rate-limiting step (RLS) is the hydride transfer from HBpin to Pd. The energy barrier for this step is 32.6 kcal mol^{-1}. In RLS, while HBpin acts as a hydride donor, it also plays the role of a carbonyl species receiver to transfer the hydride from Pd to the carbonyl carbon. Thus, a dual role of HBpin is observed in the reaction.

Experimental Section

General consideration

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled M. Braun glove box. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} (100 MHz) and ^{11}B{^{1}H} (128 MHz) spectra were recorded on the BRUKER ADVANCE III-400 spectrometer. All aldehydes, HBpin and amines were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals (India) Pvt. Ltd and stored in the glove box. Salicylaldehyde (E. Merck, India), o-pheny-lediamine (Aldrich, UK), and dichlorobis(triphenyl-phosphine)palladium(II) (Sigma-Aldrich) were purchased from reputed outlets and used as received. All the reagents and solvents were analytical grade (A.R. grade) and used without further modification. NMR solvent (CDCl$_3$) was purchased from Merck and distilled over molecular sieves.

Preparation of the Schiff base and palladium(II) complex (1)

Preparation of the Schiff base ligand (**H$_2$L**) has previously been reported by our group. The ligand was synthesised by the simple condensation reaction between o-phenylenediamine (0.108 g, 1 mmol) and salicylaldehyde (0.244g, 2 mmol) in a 1:2 molar ratio under reflux conditions (~60°C) in an ethanol medium. A yellowish orange–coloured crystalline product was obtained from the reaction mixture. The Schiff base was dried over CaCl$_2$ and collected in a glass vial.
Yield: 0.281 g (83.1%). IR (KBr pellet, cm^{-1}): 3437(v_{OH}), 1612 ($v_{C=N}$); UV-Vis (1×10-4 M, λ_{max}(abs), nm, ACN): 234(0.648), 269(0.579), 330(0.458); ^{1}H NMR (400 MHz, CDCl$_3$) δ_H = 12.96 (s, 2H), 8.6 (s, 2H), 6.8-7.3 (m, 12H), ppm.Anal cal. for C$_{20}$H$_{16}$N$_2$O$_2$ (**H$_2$L**): Calc. for C, 75.93; H, 5.10; N, 8.86; Found: C, 75.98; H, 5.07; N, 8.91.

The palladium(II)-salen complex (**1**) was synthesised by the addition of Pd(II) salt to H2L with a 1:1 molar ratio in MeOH-CHCl$_3$ (4:1) medium. The resultant solution was placed on a magnetic stirrer to be stirred slowly and two drops of Et$_3$N were added to the reaction mixture. The reddish-orange reaction solution was filtered and the filtrate was kept aside for slow evaporation over five days. Afterwards, bright orange-coloured crystals were separated from the reaction mixture, dried over CaCl$_2$ and collected in a glass vial. Finally,

various spectroscopic analyses were carried out to determine the structural formulation of the palladium(II)-Schiff base complex. The results are summarised as follows.
Yield of **1**: 0.120 g (75% based on metal salt). IR (KBr pellet, cm^{-1}): 3425 (v_{OH}), 2355, 1602 ($v_{C=N}$); UV-Vis (1×10–3 M, λ_{max}(abs), nm, ACN): 250 (0.8006), 316 (0.4893), 340 (0.4612), 356 (0.5103), 482 (0.2871). ^{1}H NMR (400 MHz, CDCl$_3$) δ_H = 8.56 (s, 2H), 6.6-7.9 (m, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$) = 166.55, 155.41, 143.57, 136.76, 128.68, 121.18, 117.66, 115.81 ppm. C$_{20}$H$_{14}$N$_2$O$_2$Pd (**1**): Calc. for C, 57.09; H, 3.35; N, 6.66; Found: C, 56.87; H, 3.18; N, 6.49.

Typical procedure for catalytic hydroboration of aldehydes and ketones (2a–5l)

Hydroboration of aldehydes and ketones with HBpin was performed using the standard protocol. In the glove box, 1mol % of Pd(II) catalyst (**1**) was taken and the corresponding ketone or aldehyde (1.0mmol) was added to a Schlenk tube followed by the addition of HBpin (1.0 mmol). The Schlenk tube was taken out from glove box and the reaction mixture was stirred in an oil bath at 60°C for 12 hours. Progress of the reaction was monitored using the ^{1}H NMR spectrum. A new CH$_2$ peak in the case of aldehyde and CH peak in the case of ketone indicated conversion into the corresponding derivatives. The reaction was quenched by CDCl$_3$ and 1,3,5-trimethoxybenzene was introduced as the internal standard. The products were characterised using ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and details are given in the electronic supporting information.

Typical procedure for Pd(II) complex 1–catalysed reductive amination of aldehydes with primary amines (6a–6j)

Hydroboration of aldimines with HBpin was performed using the standard protocol. The aldehyde (1 mmol) and amine (1 mmol) were taken together in a 25 mL Schlenk flask. Catalyst **1** (1mol %) was then added and the reaction mixture was stirred for three hours at room temperature. HBpin (1.1 eq.) was added to it and the reaction mixture was heated at 60 °C for 12 hours. After the specified time, small quantities of silica and methanol were added and the reaction mixture was again heated at 60 °C for six hours for further hydrolysis. The corresponding products obtained were isolated and purified using column chromatography. The isolated products were characterised using ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and details are given in the electronic supporting information.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

Crystallographic data and ^1H,$^{13}C\{^1H\}$ NMR spectra pertaining to complex **1,** boronate esters **2a–2j**, **3a–3g**, **4a–4d**, **5a–5l**, and secondary amines **6a–6k** are given in the electronic supporting information, which also includes computational details.

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