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ARTICLE

Aluminium complex as an efficient catalyst for chemo-selective reduction of amides to amines

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We report an efficient protocol for the catalytic chemo-selective reduction of *tert*-amides with pinacolborane (HBpin) to afford corresponding amines in high yield using aluminium complexes [κ^2-{$Ph_2P(X)NC_9H_6N$}$Al(Me)_2$] [X = S (**2a**), Se (**2b**)] as pre-catalysts at room temperature. The aluminium complexes were prepared from the reaction of [$Ph_2P(X)NC_9H_6N$] [X = S (**1a**), Se (**1b**)] and trimethylaluminium in toluene. The solid-state structure of complex **2b** is established. Tertiary amides with a wide array of electron-withdrawing and electron-donating functional groups were easily converted to the desired products through the selective cleavage of the amides' C=O bond by aluminium hydride as an active species. A kinetic study of the catalytic reaction is also reported.

Introduction

There is an ever-increasing demand for efficient catalytic reduction of amides to amines under mild conditions, since it represents a highly desired transformation in organic chemistry, agrochemical and materials chemistry, as well as the pharmaceutical field.[1,2] Due to this, development of numerous strategies for synthesis of amines continues to attract interest from chemists.[3] Reductive transformations of amides to amines are among the most straightforward methods of amine synthesis, since the starting materials can be readily accessed synthetically, as well as being naturally and predominantly available among biological molecules.[4–6] Therefore, numerous transition-metal and main-group metal complexes enjoy a pre-eminent place as homogeneous and heterogeneous catalysts in the reduction of amides,[7] including deoxygenation of amides,[8–13] hydrogenation of amides and imines.[14–17] Among the various types of catalytic hydrogenation systems, ruthenium,[18] rhodium,[19] palladium,[20] platinum, and[21] iridium[22] have shown high efficiency, but these elements are expensive and susceptible to possible constraints in terms of supply due to their geological scarcity. Although the catalytic hydrogenation pathway is highly in demand due to its atom economy, most amide hydrogenation necessitates conditions such as elevated pressure and temperature (>150 °C) to compel the reaction, which makes this process unfavourable. On the other hand, using stoichiometric quantities of traditional aluminium hydride[23] ($LiAlH_4$) and boron hydrides (B_2H_6 or BH_3·THF)[24] to achieve amide reduction is already well reported. However, clear drawbacks of these reagents are their sensitivity to air and moisture, attendant formation of environmentally hazardous waste materials, as well as lack of selectivity in the presence of various functional groups. Catalytic hydrosilylation of amides, using a range of precious-metal catalysts such as Pt,[25] Ir,[26] Rh,[27] and Ru,[28] is also well reported in the literature. Given that high selectivity and broad tolerance towards the presence of other functional groups are important factors for the acceptance and application of a given catalytic process, a new methodology with inexpensive and environment-friendly catalysts is still necessary to address the challenges faced during amide reduction.

Catalytic hydroboration of amides with pinacolborane (HBpin) has not been explored much – except recently and only in case of a reduction of carbonyl moieties[29] – and needs considerable development. As the starting material, HBpin does not react with secondary and tertiary amides at room temperature, and also shows good selectivity and functional group tolerance. Thus, it is preferable to use HBpin for the catalytic reduction of tertiary and secondary amides to amines.

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Electronic Supplementary Information (ESI) available: Text giving experimental details for the catalytic reactions, ^1H, $^{13}C\{^1H\}$ and spectra of amines **3a – 3zb,** and **4a – 4i** and compounds, **1a, 1b, 2a, 2b** in Supporting Information. For crystallographic details in CIF see DOI: 10.1039/b000000x/.

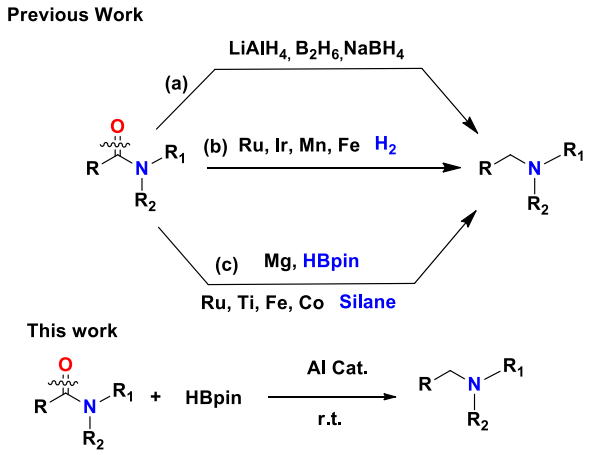
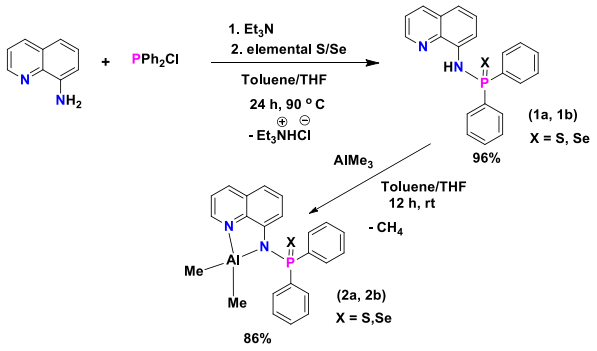


Figure 1. Previous reports for amide reduction.

Recently, Sadow et al. reported the magnesium-catalysed (ToMMgMe) hydroboration of amides by deoxygenation to amines, but the substrate scope of the reaction is very limited.[30] Our research group has reported that a number of earth-abundant materials and metals, such as alkali, alkaline earth metals,[31] titanium,[32] and aluminium[33] can be used as novel catalysts for the hydroboration of a number of carbonyl compounds including aldehydes, ketones, and carboxylic acids, followed by organic nitriles and unsaturated substrates. Due to the earth-abundant nature of the above-mentioned metal complexes, as well as the fact that they are inexpensive, easily accessible, biocompatible, and have low toxicity, these metal complexes are attractive options for various types of catalytic hydroboration of C–X unsaturated bonds. In continuation of our Al mediated catalytic hydroboration reaction,[33] we extended this protocol to amide moieties. In this paper, we report the use of aluminium bis-alkyl complexes [κ^2-{$Ph_2P(X)NC_9H_6N$}$Al(Me)_2$] [X = S (**2a**), Se (**2b**)] supported by functionalised amidophosphine ligands as an efficient protocol for the catalytic chemo-selective reduction of *tert*-amides with HBpin to afford corresponding amines in high yield at room temperature. To the best of our knowledge, this paper describes the first example of catalytic hydroboration of amides using earth-abundant aluminium.

Results and discussion

Synthesis of ligands. Aminophosphine-chalcogenide ligands [$Ph_2P(X)NHC_9H_6N$] (X = S; **1a**, Se; **1b**) were synthesised in good yield using a protocol similar to that reported in literature, that is, by the reaction of 8-aminoquinoline with chloro-diphenylphosphine (1:1 equiv.) in the presence of trimethylamine (1.5 equiv.) in a mixture of toluene and THF (1:1) followed by the addition of elemental sulphur or selenium (1.2 equiv.) in 90° C (Scheme 1).[34–35] Both ligands **1a** and **1b** were characterised using multinuclear NMR and combustion analysis, and their solid-state structures were established by single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of P–N chalcogenide ligands and Al complexes **1a**, **1b**, **2a**, and **2b**.

In the ^{1}H NMR spectra of ligands **1a** and **1b**, the signal for the amine N*H* hydrogen atom appears as a doublet at δ_H = 7.86 ppm (**1a**) and 7.81 ppm (**1b**) due to coupling with the phosphorus atom ($^2J_{HP}$ of 3.6 Hz) (Figure FS 1 and 4 in ESI). In the ^{31}P NMR spectra, ligand **1a** exhibits a sharp singlet at δ_P = 51.3 ppm and ligand **1b** displays a sharp singlet at δ_P = 47.5 ppm along with two satellite peaks due to coupling with the adjacent selenium atom. (Figure FS 3 and 6 in ESI). The solid-state structures of ligands **1a** and **1b** were established by single-crystal X-ray diffraction. Their molecular structures are given in Figures 2 and 3. The P–S bond distance in **1a** is 1.9392(10) Å and the P–Se bond distance in **1b** is 2.0981(9) Å, which are very similar to those previously reported for [$Ph_2P(S)NHCPh_3$] [1.9472(7) Å][34] and [$Ph_2P(Se)$-$NH(2,6\text{-}Me_2C_6H_3)$)] [2.1019(8) Å][35] respectively, and are hence diagnostic of double bonds (P=S and P=Se). The P–N bond distances of 1.670(2) Å and 1.672(3) Å correspond to those measured in other phosphinamines.[36-37]

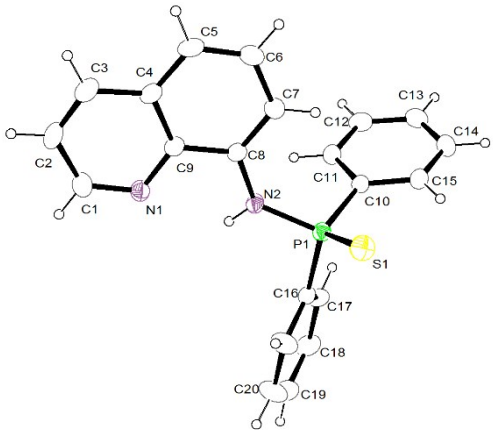


Figure 2. Molecular structure of ligand **1a** in the solid state. Selected bond lengths (Å) and angles (deg) are given. P1–N2 1.670(2), P1–S1 1.9392(10), P1–C10 1.808(3), P1–C16 1.809(2), N2–P1–S1 115.91(8), N2–P1–C16 100.39(11), N2–P1–C10 104.90(12). CCDC No. 1912620.

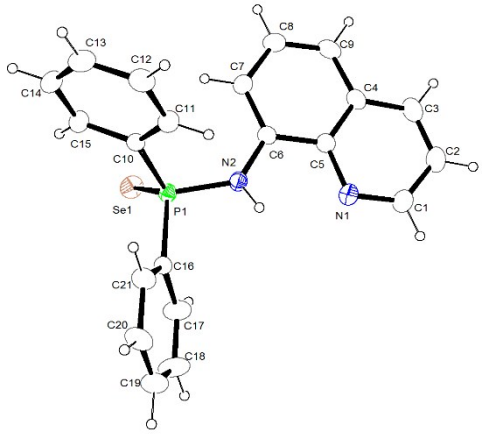


Figure 3. The molecular structure of ligand **1b** in the solid state. Selected bond lengths (Å) and angles (deg) are given. P1–N2 1.672(3), P1–Se1 2.0981(9), P1–C10 1.807(3), P1–C16 1.798(3), N2–P1–Se1 115.99(10), N2–P1–C16 100.87(14), N2–P1–C10 105.15(14). CCDC No. 1912619.

Synthesis of Aluminium complexes. Trimethylaluminium was reacted with one equivalent of aminophosphinchalcogenides $[Ph_2P(X)NHC_9H_6N]$ to afford, in good yield (Scheme 1), corresponding aluminium complexes $[\kappa^2\text{-}\{Ph_2P(X)NC_9H_6N\}Al(Me)_2]$ [X = S (**2a**), Se (**2b**)] as colourless solids. Both the Al complexes showed good solubility in common organic solvents such as THF and toluene. Complexes **2a** and **2b** were characterised using ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectral data, and combustion analysis. The solid-state structure of complex **2b** was established by single-crystal X-ray crystallography. In the ^1H NMR spectra of complexes **2a** and **2b** measured in C_6D_6, the absence of a doublet resonance signal at 7.86 ppm and 7.81 ppm assigned to the –NH proton of ligands **1a** and **1b** respectively confirms the formation of the monoanionic fragment of ligand **1a** and **1b** respectively. Complexes **2a** and **2b** display two sharp singlets at δ_H = –0.186 ppm and –0.416 ppm respectively in respect of resonance signals of the two methyl groups attached to the metal ions (Figures FS 7 and 10 in ESI). Additionally, in the $^{31}P\{^1H\}$ NMR spectra, complexes **2a** and **2b** exhibit resonance signals at δ_P = 64.6 ppm and 58.2 ppm respectively, which are significantly downfield shifted compared to the signals of the corresponding ligands, which are δ_P = 51.3 ppm (**1a**) and 47.5 ppm (**1b**) (Figures FS 8 and 11 in ESI).

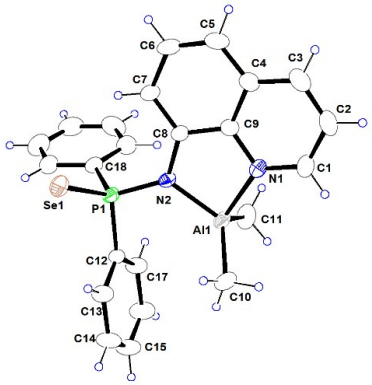
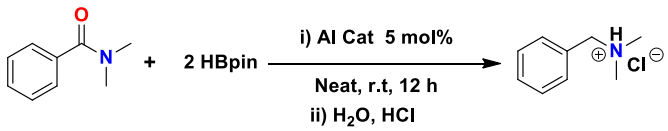


Figure 4. The molecular structure of aluminium complex **2b** in the solid state. Selected bond lengths (Å) and angles (deg) are given. Al1–N1 1.963(5), Al1–N2 1.909(5), Al1–C10 1.955(7), Al1–C11 1.955(7), N2–P1 1.656(5), P1–Se1 2.1093(17), N1–Al1–N2 84.88(19), N1–Al1–C10 109.8(3), N1–Al1–C11 104.0(3), N2–Al1–C10 117.5(3), N2–Al1–C11 113.3(3), Al1–N2–P1 126.7(2). CCDC No. 1912621.

As mentioned earlier, the molecular structure of complex **2b** in the solid state was confirmed by single-crystal X-ray diffraction analysis. Complex **2b** crystallises in the triclinic space group *P*-1, with two molecules in the unit cell. Crystallographic and refinement parameters are given in Table TS1. The molecular structure of complex **2b** is depicted in Figure 4. The solid-state structure of complex **2b** confirms the ligation of two aminophosphine-selenide ligands to the Al ion through anionic phosphinamido nitrogen and the nitrogen atom of the 8-aminoquinoline moiety of ligand **1b**. The selenium atom remains non-coordinated. Additionally, two methyl groups are attached to the aluminium ion, resulting in a distorted tetrahedral geometry around the metal centre. Two sets of Al–N distances, 1.909(5) Å and 1.963(5) Å, are consistent with the distances of the anionic amido–Al and neutral nitrogen–Al bonds in the ligand **1b** and are within the range that we previously reported for complex $[\kappa^2\text{-}\{2\text{-}F\text{-}C_6H_4NP(Se)Ph_2\}_2Al\text{-}(Me)]$ and other reported Al complexes.[32]

Catalytic reduction of amides. After successful synthesis of the two aluminium complexes **2a** and **2b**, we tested them as pre-catalysts for the selective reduction of tertiary amides with HBpin to afford the corresponding amines. The reduction of N,N-dimethyl benzamide with HBpin in the presence of 5 mol% of complex **2a** or complex **2b** at room temperature was chosen as the model reaction (Table 1). First, we tested the reaction in the absence of the catalyst, which did not afford any amine, thus confirming the necessity of the catalyst (Table 1, entry 1). However, reactions using complexes **2a** and **2b** as catalysts under solvent-free conditions afforded high yields – 84% and 88% respectively – within 12 hours (Table 1, entries 2–3). Extending the reaction time to 24 hours when using complex **2b** as the catalyst increased the yield of the product to 94% (Table 1, entry 4). Hence, complex **2b** was chosen as the best catalyst. With the selected catalyst **2b**, we examined the effect of solvent on the selective reduction of N,N-dimethyl benzamide by HBpin, for which various solvents such as toluene, THF, and hexane, were screened. However, in all cases, we observed slow reactivity even after lengthy reaction times (Table 1, entries 5–7). Further, catalyst loading of 2.5% or 1% substantially lowered the reaction rate, and yields of 70% and 62% respectively were observed after 12 hours of the reaction (Table 1, entries 8–9). We increased the molar ratio of HBpin to four equivalents with respect to the N,N-dimethylbenzamide; however, no significant increase in yield was observed (Table 1, entry 10). Therefore, we set out to examine the scope of various substrates of *tert*-amide, with room temperature and solvent-free conditions taken as optimal, in the presence of 5 mol% of the aluminium complex **2b**.

Table 1. Screening of Al complexes as a pre-catalysts for reduction of *tert*-amide to yield the corresponding amine.

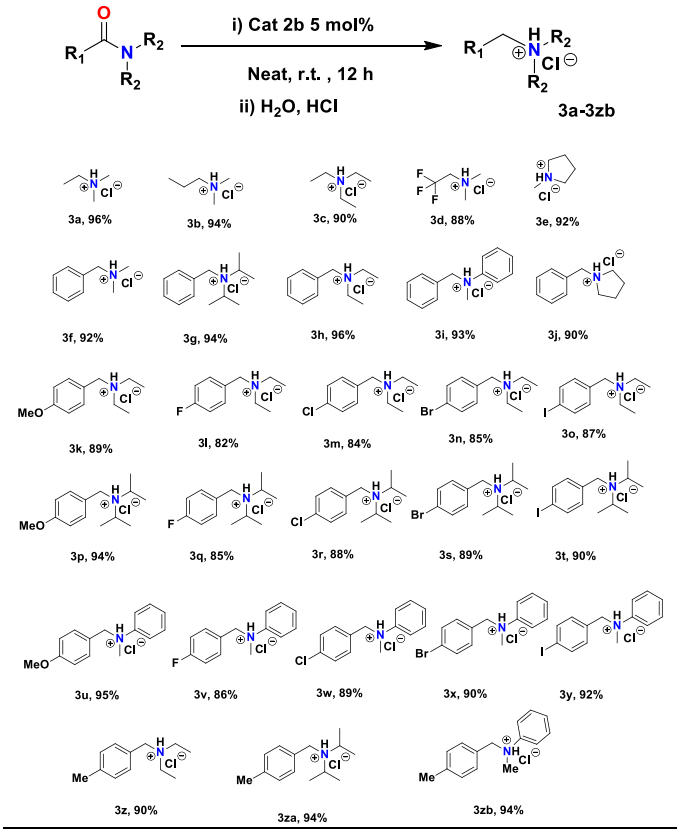


Entry	Catalyst	Solvent	Cat (X mol)	t (h)	T (°)	Yield[a](%)
1	None	Neat	-	12	RT	0
2	**2a**	Neat	5	12	RT	84
3	**2b**	Neat	5	12	RT	88
4	**2b**	Neat	5	24	RT	94
5	**2b**	Toluene	5	24	RT	69
6	**2b**	THF	5	24	RT	65
7	**2b**	Hexane	5	24	RT	58
8[b]	**2b**	Neat	2.5	12	RT	70
9[c]	**2b**	Neat	1	12	RT	62
10[d]	**2b**	Neat	5	24	RT	92

[a]Isolated yield. [b,c]Reaction was performed using 2.5 mol% (entry 8) and 1 mol% (entry 9) of catalyst **2b**, [d]Reaction was performed using molar ratio of HBpin : N,N-dimethylbenzamid = 4:1.

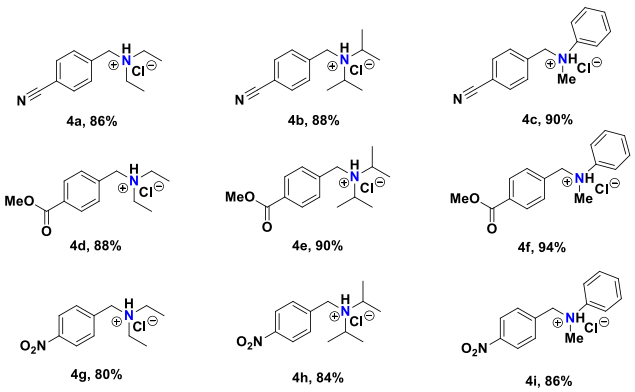
With these optimised conditions, we first investigated the scope of the reaction in the presence of aliphatic, aromatic as well as heterocyclic amides with HBpin. Table 2, which summarises the results, indicates that all the aliphatic, aromatic, and heterocyclic amides are reduced smoothly under the optimised reaction conditions with HBpin (Table 2, entries **3a–3zb**). In each case, the yield of the corresponding amine product was isolated, and then the yield was calculated (Figures FS 13–95 in ESI). The reduction of N, N-dimethylacetamide proceeded rapidly and a quantitative yield (96%) of N, N-dimethyl ethanamine was obtained within five hours (Table 2, entry 3a). Similarly, N, N-dimethyl propionamide, N,N-diethyl acetamide and N-methyl pyrrolidine-2-one gave excellent yields (>90%) of the corresponding amines at room temperature (Table 2, entries **3b**, **3c**, and **3e**) (Figures FS 15–20 and FS25–27 in ESI). When 2,2,2-trifluoro-N,N-dimethylacetamide was used as the substrate, we were pleased to find that 88% of the product was obtained under similar conditions, indicating that the electron-withdrawing trifluoro group has no significant impact on the reaction (Table 2, entry **3d**) (Figures FS 21–24 in ESI). Aryl amides with no substitution in the benzene ring, such as N,N-dimethyl-benzamide, N,N-diisopropyl benzamide, N,N-diethyl benzamide, N-methyl-N-phenyl benzamide, and phenyl-(pyrrolidine-1-yl)methanone reduced smoothly, producing the corresponding *tert*-amines in nearly quantitative yields (Table 2, entries **3f–3j**) (Figures FS 28–42 in ESI). To explore the electronic effect of the amide reduction reaction, we treated a series of differently substituted benzamides where substitution on the nitrogen atom was varied from ethyl, isopropyl, and methyl-phenyl groups and substitution on the *para*-position of the benzene ring was changed from electron-donating groups such as methoxy to electron-withdrawing ones, such as fluoro, chloro, bromo, and iodo groups. We observed that the presence of electron-donating groups at the *para*-position of the benzene ring resulted in higher yields than the presence of the corresponding halide-substituted amides (Table 2, entries **3k–3Zb**) (Figures FS 43–95 in ESI).

Table 2. Substrate scope for reduction 3° amide to corresponding amine synthesis catalysed by complex **2b**.



All reactions were performed in the neat condition under ambient temperature for 12 hours using different amides (0.5649 mmol, 1 equiv.), HBpin (1.129 mmol, 2 equiv.), and complex **2b** (22 mg, 0.02824 mmol, 5 mol%). Yields were calculated as an isolated yield basis.

Table 3. Chemo-selective catalytic reduction of 3° amide by catalyst **2b**.

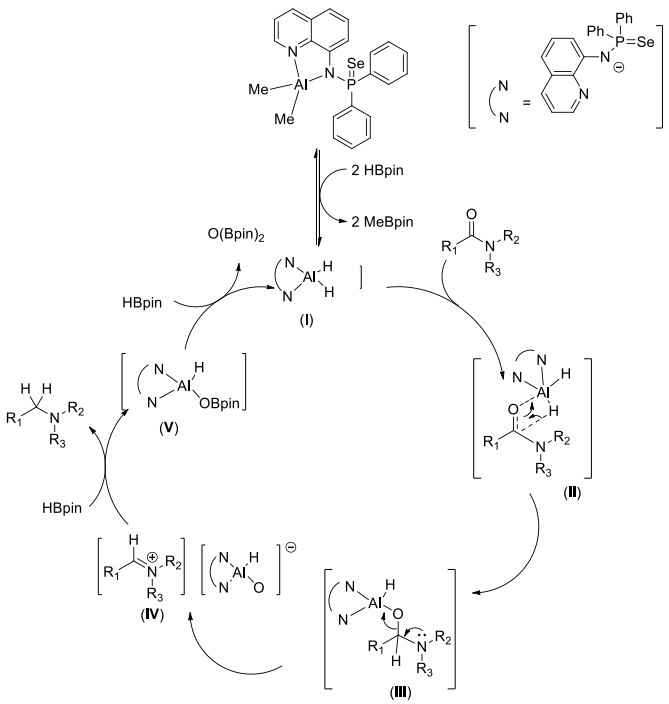


All reactions were performed in the neat condition under ambient temperature for 12 hours using different amides (0.5649 mmol, 1 equiv.), HBpin (1.129 mmol, 2 equiv.), and complex **2b** (22 mg, 0.02824 mmol, 5 mol%). Yields were calculated as an isolated yield basis.

After demonstrating the general applicability of our procedure, we wanted to investigate the functional group tolerance and chemo-selectivity of the catalytic system. Thus, we studied particularly challenging substrates, which we estimated might undergo additional reductive transformations in the presence of HBpin. To our delight, in each case, only the amide moieties reduced, while the additional ester, ether, nitro, cyano, and non-conjugated double bonds remained intact, representing the high chemo-selectivity of the aluminium complexes (Table 3, entries **4a**–**4i**) (Figures FS 96–122 in ESI). All the results are summarised in Table 3.

Kinetic Study. To determine the initial rate of catalytic reduction of amines, kinetic experiments were performed with respect to the starting material and catalyst **2b**. Reactions were performed with varied concentrations of catalyst **2b**, as well as N,N-dimethyl benzamide and HBpin while keeping the concentration of other reagents unchanged. Hence, in situ NMR experiments were carried out by loading complex **2b** (0.03, 0.04, 0.05, 0.06, 0.07 M) from a stock solution and adding N,N-dimethyl benzamide (0.126 g, 1.0 mmol), HBpin (0.108 g, 1.0 mmol), and C_6D_6 (1 mL) to it. The temperature of the solution mixture was set at 60°C. At indicated time intervals, the solution was analysed by ^{1}H NMR, which revealed that the rate law of the reactions displays a first-order dependence on complex **2b** (Figures FS123–FS126 in ESI). Increasing the amount of N,N-dimethyl benzamide and HBpin also displayed first-order dependence on N,N-dimethyl benzamide (Figure FS127 in ESI), HBpin (Figure FS 128 in ESI). Hence, the overall rate of the reaction gave rise to the following kinetic rate equation:

$$dp/dt = k_{obs}\,[\text{N,N-dimethylbenzamide}]^1.\,[\text{HBpin}]^1.\,[\mathbf{2b}]^1$$



Scheme 2. Proposed mechanism for the selective reduction of amides to amines.

The proposed mechanism for the catalytic hydroboration of amide with HBpin is shown in Scheme 2. Initially, the aluminium pre-catalyst **2b** reacts with HBpin to form the active aluminium hydride species (**I**), which further reacts with one equivalent of the amide, during which the nucleophilic hydride ion attacks the carbonyl carbon of the amide, producing a tetrahedral intermediate (**III**). Complex (**III**) eventually rearranges itself to give the iminium species (**IV**), which further reacts with another molecule of HBpin to yield the amine product as well as the boryl aluminium species (**V**). In the final step, the active aluminium hydride species is regenerated using another molecule of HBpin, by eliminating the corresponding free dioxaborolane product. No decomposition of HBpin was observed during the reaction.

Conclusions

We have demonstrated the synthesis of two aluminium complexes, **2a** and **2b**, stabilised by the quinoline-based amino-phosphinechalcogenide ligand. The solid-state structure of complex **2b** is established. Aluminium complex **2b** was used as a pre-catalyst for the catalytic chemo-selective reduction of 3° amides with HBpin to afford corresponding amines in high yields at room temperature. Catalyst **2b** exhibited high conversion, superior selectivity, and broad functional group tolerance during the reaction.

Experimental

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. All the amides were prepared according to the published procedure.[22] The NMR solvent C_6D_6 was purchased from Sigma Aldrich. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1912620 (**1a**), 1912619 (**1b**) 1912621 (**2b**).

Preparation of $[Ph_2P(X)NC_9H_6N]$ [X = S (1a), Se (1b)]. In a dry 25 mL Schlenk flask, a mixture of 8-aminoquinoline (500 mg, 3.472 mmol) and 25 mL of toluene/THF was placed. To this solution, chlorodiphenylphosphine (765 mg, 3.472 mmol) was added, after which trimethylamine (527 mg, 5.208 mmol) was also added. The resulting reaction mixture was stirred continuously for 12 hours at room temperature. A white precipitate was obtained, which was filtered, and the filtrate was collected into another dry Schlenk flask. Elemental sulphur (166 mg, 5.208 mmol for ligand **1a**) or selenium (401 mg, 5.208 mmol for ligand **1b**) was added to it and the reaction mixture was heated at 90°C for 24 hours. Then the solution was

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filtered and the solvent was evaporated under vacuum, resulting in an oily compound which was washed with *n*-hexane. The title compound was re-crystallised from THF/toluene at –35ºC and colourless crystals were obtained after three days.

1a: Yield: 1.20 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 8.73 - 8.71 (dd, 1H $^{1}J_{HH}$ = 3.6, 1.2 Hz, Ar), 8.11 - 8.06 (m, 4H, Ar), 7.86 (d, 1H N*H*), 7.54 - 7.45 (m, 5H, Ar), 7.41 - 7.38 (m, 1H, Ar) 7.32 - 7.24 (m, 3H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 147.9 (Ar), 139.2 (Ar), 137.3 (Ar), 136.3 (Ar), 133.0 (Ar), 131.6 (Ar), 128.9 (Ar), 126.8 (Ar), 121.7 (Ar) 119.2 (Ar), 114.0 (Ar), ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ_P = 51.3 ppm. Elemental Analysis: $C_{21}H_{17}N_2PS$ (360.41): Calcd. C 69.98, H 4.75, N 7.77. Found C 69.71, H 4.53, N 7.47.

1b: Yield: 1.34 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ_H 8.72 - 8.70 (dd, 1H $^{1}J_{HH}$ = 4.2, 1.5 Hz, Ar), 8.11 - 8.05 (m, 4H, Ar), 7.81 (d, 1H N*H*), 7.51 - 7.44 (m, 5H, Ar), 7.40 - 7.37 (m, 1H, Ar) 7.33 - 7.27 (m, 3H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 147.9 (Ar), 139.2 (Ar), 137.3 (Ar), 136.3 (Ar), 133.0 (Ar), 131.6 (Ar), 128.9 (Ar), 126.8 (Ar), 121.7 (Ar) 119.2 (Ar), 114.0 (Ar), ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ_P = 47.5 ppm. Elemental Analysis: $C_{21}H_{17}N_2PSe$ (407.30): Calcd. C 61.92, H 4.21, N 6.88. Found C 61.58, H 4.11, N 6.64.

Preparation of [κ^2-{$Ph_2P(X)NC_9H_6N$}$Al(Me)_2$] [X = S (2a), Se (2b)]. In a dry 25 mL Schlenk flask, ligand **1a** (200 mg, 0.555 mmol) or **1b** (200 mg, 0.4914 mmol) and 5 mL of toluene were added. To this solution, trimethylaluminium (40.04 mg, 0.555 mmol) (**2a**) or (35.4 mg, 0.4914 mmol) (**2b**) was added, and the resulting reaction mixture was stirred continuously for 12 hours at room temperature. The solvent was then evaporated under vacuum to produce a yellow-coloured residue, which was dissolved in 3 mL of toluene and set aside for re-crystallisation at –35ºC. Yellow-coloured crystals were obtained after three days.

2a: Yield: 73 mg, 88%. ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ_H 8.21 - 8.15 (m, 4H, Ar), 7.69 - 7.68 (dd, 1H, $^{1}J_{HH}$ = 4.6 Hz, Ar), 7.31 - 7.24 (m, 1H Ar), 7.15 - 7.11 (m, 1H, Ar), 7.06 - 7.00 (m, 7H, Ar) 6.84 - 6.80 (t, 1H, Ar) 6.58 - 6.56 (d, 1H, $^{1}J_{HH}$ = 8.2 Hz, Ar), 6.43 - 6.40 (m, 1H, Ar), -0.18 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 143.8 (Ar), 139.7 (Ar), 135.3 (Ar), 134.4 (Ar), 132.5 (Ar), 131.3 (Ar), 129.5 (Ar), 128.9 (Ar), 128.4 (Ar) 127.9 (Ar), 125.5 (Ar), 121.3 (Ar), 115.4 (Ar), 67.7 (*C*H$_3$), 25.6 (*C*H$_3$), 21.2 (*C*H$_3$) ppm. ^{31}P {^{1}H} NMR (161.9 MHz, C_6D_6): δ_P = 64.6 ppm. Elemental Analysis: $C_{27}H_{30}AlN_2OPS$ (488.56): Calcd. C 66.38, H 6.19, N 5.73. Found C 66.11, H 5.89, N 5.51.

2b. Yield: 84 mg, 88%. ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ_H 8.24 - 8.19 (m, 4H, Ar), 7.62 - 7.61 (d, 1H $^{1}J_{HH}$ = 4.7 Hz, Ar), 7.45 - 7.43 (m, 1H Ar), 7.26 - 7.24 (m, 1H, Ar), 7.02 (m, 6H, Ar) 6.84 - 6.80 (t, 1H, Ar) 6.58 - 6.56 (d, 1H $^{1}J_{HH}$ = 8.2 Hz, Ar) 6.43 - 6.40 (m,1H, Ar), -0.26 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 143.7 (Ar), 139.9 (Ar), 134.7 (Ar), 132.8 (Ar), 131.3 (Ar), 129.5 (Ar), 128.9 (Ar), 128.4 (Ar) 127.9 (Ar), 121.3 (Ar), 118.1 (Ar), 115.6 (Ar), 67.7 (*C*H$_3$), 25.6 (*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ_P = 58.2 ppm. Elemental Analysis: $C_{27}H_{30}AlN_2OPSe$ (535.46): Calcd. C 60.56, H 5.65, N 5.23. Found C 60.32, H 5.49, N 5.10.

General procedure for catalytic aluminium complex-mediated reduction of amides with HBpin.

The required amide precursor (0.5649 mmol, 1 equiv.) was added to the reaction mixture of HBpin (1.129 mmol, 2 equiv.) and 5 mol% ligand **1a** (22 mg, 0.02824 mmol). This was done in a 25 mL dry Schlenk flask inside a glovebox. The colourless reaction mixture was stored at room temperature or heated to 40–60°C, depending on the nature of nucleophiles. After 12 hours, the reaction mixture was quenched with a 4N HCl acid workup for four–five hours, and then washed with dichloromethane two–three times. Subsequently, the aqueous part of the reaction mixture was evaporated using a rotary evaporator, and a colourless product was obtained. The products were identified according to ^{1}H, ^{13}C, and DEPT NMR spectroscopy (where necessary), as well as MS analysis.

Conflicts of interest

There are no conflicts to declare.

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Aluminium complex as an efficient catalyst for chemo-selective reduction of amides to amines

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Graphical Abstract

Catalytic chemo-selective reduction of *tert*-amides with pinacolborane (HBpin) to furnish corresponding *tert*-amines using earth abundant Al complex under solvent free, base free and mild conditions is reported.