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ARTICLE

Alkali Metal Complexes as Efficient Catalysts for Hydroboration and Cyanosilylation of Carbonyl Compounds

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We report here reactions between the *N*-adamantyliminopyrolyl ligand 2-(AdN=CH)-C_4H_3NH (**L–H**) and alkali metal hexamethyldisilazides [MN($SiMe_3$)$_2$] (M = Li, Na and K) to afford the dimeric [{2-(AdN=CH)-$C_4H_3NLi(THF)$}$_2$] (**1**), [{2-(AdN=CH)-C_4H_3N}$Na(THF)_{1.5}$}$_2$] (**2**) and polymeric [{2-(AdN=CH)-$C_4H_3NK(THF)$}$_n$] (**3**) complexes at ambient temperature. A one-pot reaction between **L–H**, [KN($SiMe_3$)$_2$] and alkaline earth metal diiodide (AeI_2) in a 2:2:1 molar ratio, which resulted in the formation of a heteroleptic Ae metal complex [κ^2-{2-(AdN=CH)-C_4H_3N}$_2$Ae$(THF)_2$] [Ae = Mg (**4**), Ca (**5**)] is also reported. The solid-state structures of complexes **1**, **3** and **4** were established through single-crystal X-ray diffraction analysis. The alkali and alkaline earth metal complexes **1**–**5** were utilised as precatalysts for the catalytic hydroboration of pinacolborane (HBpin) with aldehydes and ketones and potassium complex **3** was identified as a competent catalyst under mild conditions. Additionally, cyanosilylation of carbonyl compounds was explored with trimethylsilyl cyanide and aldehyde/ketones, using the alkali metal precatalyst **3** under mild conditions. In both catalytic processes, the potassium catalyst **3** exhibited a high tolerance towards a number of functional groups. First-order kinetics with respect to catalyst **3** and each of the substrates was observed for the hydroboration reaction of carbonyl compounds catalysed by alkali metals.

Introduction

In present-day synthetic organic chemistry, the adoption of atom-economical and eco-friendly chemical processes is one of the most essential topics in research.[1-3] In particular, finding relatively less toxic and harmless alternatives for metals that have toxic and detrimental effects on the environment is highly desirable.[4-9] Furthermore, the use of abundant metals is encouraged, rather than rare metals, because of the latter's potential for becoming depleted in future. Group 1 metals such as lithium, sodium and potassium are recognised as being among the most abundant elements in nature, but their application in synthetic chemistry is limited.[10-15] Over the past few years, several research groups have been keen to explore the catalytic activity of alkali metals (AMs) in various catalytic transformations: Gange *et al.* reported transesterification mediated by AM oxides,[16] the Song group explored the synthesis of alkyl borates mediated by AM carbonates,[17] Zaho *et al.* reported the hydroboration of carbonyl compounds using AM hydroxides,[18] Grubbs *et al.* reported C–H bond silylation using AM hydroxides and AM aldoxides,[19-23] while Wu *et al.* described a highly selective catalyst (mediated by AM alkoxide) for the ring-opening polymerisation of lactides. Additionally, [24] Hill *et al.*, R. Muley *et al.* and our group also reported active cross-dehydrogenative coupling of NH/BH, NH/SiH, and OH/SiH using AM complexes.[25-30] Although an extensive array of transition-metal catalysts have been explored in the hydroboration of carbonyl compounds,[31] very limited AM-based catalysts have been reported till date. Certain selected alkali and alkaline earth metal catalysts known for hydroboration of carbonyl compounds are given in Fig 1.[32-40]

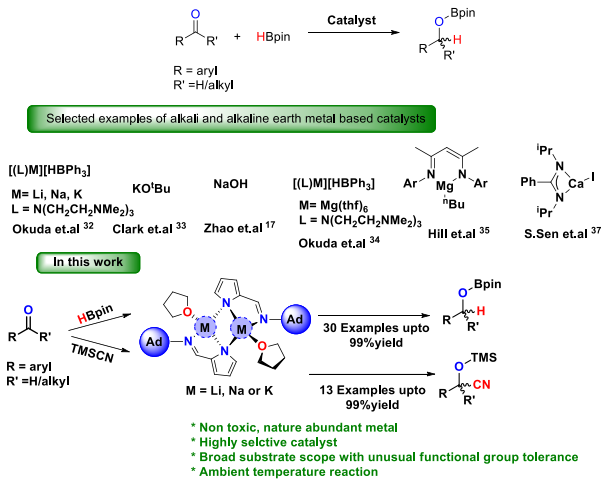

Figure 1. Selected alkali and alkaline earth metal catalysts reported in literature.

In our ongoing research on alkali and alkaline earth metal chemistry, we have developed a wide range of related catalyst systems for various organic transformations.[41-43] In continuation of that

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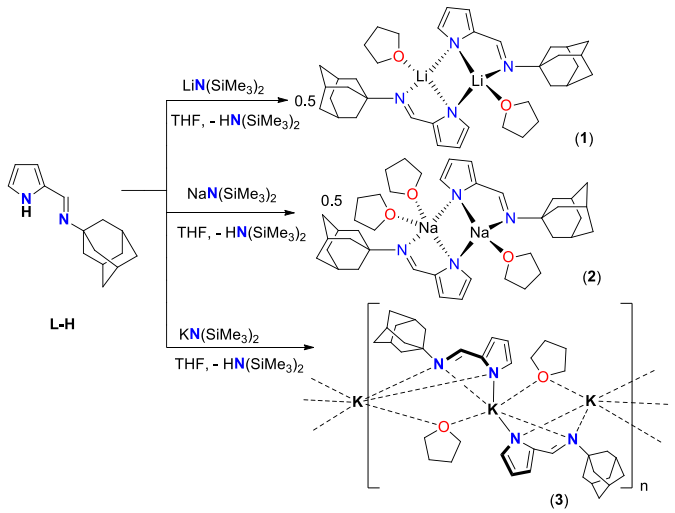
Electronic Supplementary Information (ESI) available: Text giving X-ray diffraction analysis, crystallographic table, ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and spectra of products obtained from catalytic reaction are given in Supporting Information.. See DOI: 10.1039/x0xx00000x

research, we wanted to introduce a competent AM catalyst for the hydroboration of carbonyl compounds, which exhibits greater efficiency and higher tolerance towards various active functional groups. In this context, we report here the synthesis and structural details of *N*-adamantyl iminopyrolyl alkali metal complexes of molecular formulae [{2-(AdN=CH)-$C_4H_3NLi(THF)\}_2$] (**1**), [{2-(AdN=CH)-$C_4H_3N\}Na(THF)_{1.5}\}_2$] (**2**) and [{2-(AdN=CH)-$C_4H_3NK(THF)\}_n$] (**3**) and heteroleptic alkaline earth (Ae) metal complex [κ^2-{2-(AdN=CH)-$C_4H_3N\}_2Ae(THF)_2$] [Ae = Mg (**4**), Ca (**5**)]. We also describe the catalytic efficiency of the potassium complex **3** as a pre-catalyst for the catalytic hydroboration and cyanosilylation with aldehydes and ketones.

Results and discussion

Syntheses and structures of alkali metal complexes. The N-adamantyl iminopyrolyl ligand **L–H** was prepared by the condensation reaction between adamantylamine and 2-pyrrole carboxaldehyde.[44] The solid-state structure of the hydrochloride salt of the ligand (**L–H**.HCl) is given in the supporting information. Alkali metal (Li, Na and K) complexes with molecular formulae [{2-(AdN=CH)-$C_4H_3NLi(THF)\}_2$] (**1**), [{2-(AdN=CH)-$C_4H_3N\}Na(THF)_{1.5}\}_2$] (**2**) and [{2-(AdN=CH)-$C_4H_3NK(THF)\}_n$] (**3**) were prepared from the reactions between the protic ligand **L–H** and [$MN(SiMe_3)_2$] (M = Li, Na, K) in THF through elimination of the volatile hexamethyldisilazane (Scheme 1). All three complexes were characterised using spectroscopic and analytical techniques, and their solid-state structures were confirmed by single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of lithium, sodium and potassium complexes **1–3**.

All the three complexes **1–3** show sharp resonance signals at δ_H 8.26 (for **1**), 7.96 (for **2**) and 8.16 ppm (for **3**) in the ^{1}H NMR spectra measured in C_6D_6 due to the presence of an imine proton (N=CH) in the ligand moiety. Two multiplet signals, at δ_H 1.43–1.40 and 3.59–3.56 ppm, were observed in each complex, which confirmed the presence of coordinated THF molecules in each compound. The resonance signals of the pyrrolyl protons of all the above-mentioned alkali metal complexes appeared in the expected region.[45] The $^{13}C\{^1H\}$ NMR spectra also indicated the presence of an imine carbon atom in each complex, which exhibited resonance signals at δ_c 151.6 (for **1**), 151.6 (for **2**) and 146.8 ppm (for **3**), and the values were similar to that of the free ligand (146.4 ppm for **1–H**).

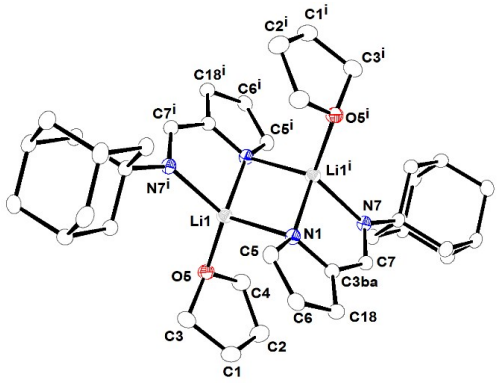


Figure 2. Solid-state structure of lithium complex **1**. Selected bond lengths (Å) and angles (deg) are given. Li1–N1 2.141(3), Li1–N7^i 2.106(5), Li1–N1^i 2.073(5), Li1–O5 1.940(5), Li1^i–N1 2.073(3), N7–Li1^i 2.106(3), N1–Li1-N1^i 104.77(14), O5–Li1–N1 107.70(14), N7^i–Li1^i -N1 120.24(14), N1–Li1–Li1^i 53.58(11), O5–Li1–N7^i 121.97(15), N1^i–Li1–Li1^i 53.58(11), N7^i–Li1–Li1^i 112.55(18).

Single crystals of complexes **1–3** were obtained from a mixture of each corresponding complex (with THF) and *n*-pentane solution. The molecular structures of **1–3** confirm the attachment of ligand **L** to the lithium, sodium and potassium ions respectively. The sodium complex **2** has higher R factors due to poor X-ray diffraction data set, and the molecular structure of complex **2** in the solid state is given in the supporting information (Fig FS2). The lithium complex **1** crystallises in the monoclinic space group *P* $2_1/c$, with two molecules in the unit cell. However, the analogous potassium complex **3** crystallises in the triclinic space group *P* -1, with two molecules in the unit cell. The details of the structural parameters are given in Table TS1 in the ESI. The solid-state structures of complexes **1** and **3** are shown in Figures 2 and 3 respectively.

Molecular structures of the lithium complex **1** and sodium complex **2** (Fig FS 2 in ESI) were found to be quite similar, as well as being dimeric in nature, when compared to the solid-state structure of the potassium complex **3**, which is polymeric in nature. In both the dimeric complexes **1** and **2**, the coordination polyhedron was formed by the ligation of the pyrrolylide and imine nitrogen atoms of the monoanionic bis-iminopyrrolyl ligand **L** to two alkali metal ions. We observed that ligand **L** formed a diamond-shaped M_2N_2 core in each case, in which the pyrrolylide nitrogen atom was chelated to the two metal ions in μ^2 coordination mode. In addition, the imine nitrogen of each ligand moiety coordinated to each metal ion, which also coordinated to one THF molecule. Thus, each lithium ion in complex **1** was four-fold coordinated and the geometry around it can best be described as a distorted tetrahedral. In sodium complex **2**, one of the sodium ions coordinated additionally with two THF molecules to make the two sodium ions non-equivalent. A distorted tetrahedral

geometry was observed around one sodium ion which was four-fold coordinated, whereas a distorted bipyramidal geometry could be obtained around the second sodium ion which was five-fold coordinated. Similar coordination for lithium and sodium are quite well known in literature.[46]

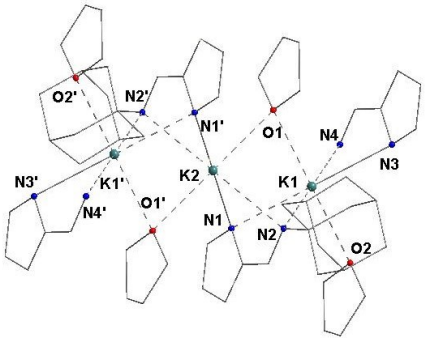
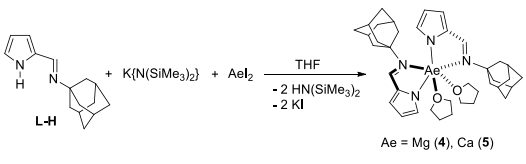


Figure 3. Solid-state structure of complex **3**. Selected bond lengths (Å) and angles (deg) are given. K1–N1 2.796(3), K1–N2^{i} 2.863(3), K1–O1^{i} 2.823(3), K1–O1^{i} 2.823(3), K1–K2 3.6717(6), K2–N1 2.786(4), K2-N2 2.854(3), K2-O2 2.8133(3), N1–K2-K1 131.06(6), N1–21–O1 91.68(10), O1–K2 -K1 130.55(7), O1–K2–N2 87.92(9), O1–Lk2–C5 102.66(9), O1^{i}–K1–K1^{i} 49.33(6), N1–K2–N2 117.02(10).

The solid-state structure of complex **3** was found to be polymeric in nature (Fig 3). The molecular structure of complex **3** confirms the κ^4 coordination of the iminopyrrolide ligand towards two adjacent potassium ions. In complex **3**, both the pyrrolide and imine nitrogen atoms are chelated to two potassium ions through a bridging coordination mode. One THF molecule is also coordinated to two metal ions trough bridging modes, making each potassium ion six-fold coordinated to adopt a distorted octahedral geometry around it. In complex **3**, the monoanionic iminopyrrolide ligand acts as a bridging ligand with κ^4 coordination mode using its two donor nitrogen atoms. The polymeric structure of complex **3**, which contrasts with the dimeric structure of complexes **1** and **2**, can be attributed to the size of the potassium ion, which is larger than the lithium and sodium ions. In complexes **1**–**3**, the M–N_{pyr} and M–N_{imin} distances are in the range of corresponding metal–nitrogen distances reported for alkali–metal iminopyrrole complexes in literature.[47]

Alkaline earth metal complexes. The heteroleptic magnesium and calcium complexes **4** and **5** were isolated in good yield in a one-pot reaction of **L–H**, [KN(SiMe$_3$)$_2$] and the corresponding metal diiodide (AeI$_2$) in a 2:2:1 molar ratio at room temperature (Scheme 2). The air- and moisture-sensitive compounds **4** and **5** were characterised by multinuclear NMR spectroscopic and combustion analysis techniques. The solid-state structure of complex **4** was established by single-crystal X-ray diffraction analysis.



Scheme 2. Synthesis of Ae metal complexes **4–5**.

In the ^{1}H NMR spectra of complexes **4** and **5**, measured in C_6D_6, the disappearance of signals at δ_H 10.58 ppm, assigned for pyrrole -NH proton, indicates the formation of monoanionic ligand fragments **L** in each complex (Figures FS5–FS12 in ESI). The resonance of the imine proton was observed as a singlet at δ_H 8.03 ppm (**4**) and 7.66 ppm (**5**). In the ^{13}C{^{1}H} NMR spectra, resonance at δ_c 146.8 ppm (for **4**) and 145.8 ppm (for **5**) can be assigned to the imine carbon (H*C*=N) present in the ligand moiety. However, these values are in accordance to that of the free ligand **L–H** (146.4 ppm).

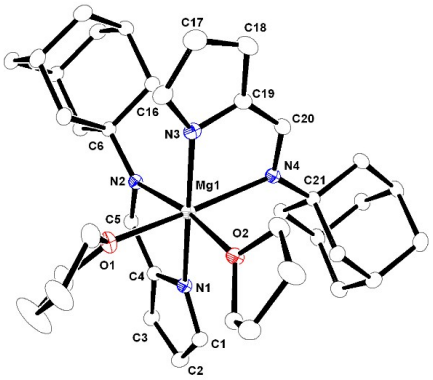
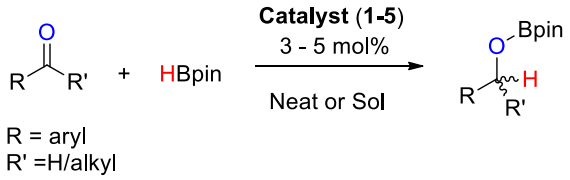


Figure 4. Synthesis of alkali metal complex **4**. Selected bond lengths (Å) and angles (deg) are given. Mg1–N1 2.143(2), Mg–N3 2.137(5), Mg1–N2 2.268(2), Mg1–N4 2.274(2), Mg1–O1 2.172(2), Mg1–O2 2.173(2), N3–Mg1–N1 177.78(9), N3–Mg1–O1 92.74(9), N1–Mg1–O2 94.51(8), O1–Mg1–O2 83.63(8), N2–Mg1–N4 98.47(8), N1–Mg1–N4 100.15(9), O1–Mg1–N2 90.15(8).

Crystals of compounds **4** and **5** were isolated from a mixture of THF and pentane solution at –35°C. The single-crystal X-ray data obtained for complex **5** was not complete, and thus a satisfactory molecular structure could not be obtained. In the molecular structure of complex **4** in the solid state, the attachment of two iminopyrrolide ligands to the magnesium ion was confirmed. Complex **4** crystallises in the monoclinic space group *P* 2$_1$/c, with four molecules in the unit cell. The details of the structural parameters are given in TS1 in the supporting information. Figure 4 represents the molecular structure of complex **4**. In complex **4**, the magnesium ion is coordinated by two iminopyrrolyl moieties through κ^2 NN mode and two THF molecules to adopt a distorted octahedral geometry around the magnesium ion. We noted that both the THF molecules are *cis* to each other. In complex **4**, we observed two sets of Mg–N distances: one short and one long. The short bond distance of 2.143(2) Å for Mg–N_{pyr} indicates the presence of larger electron density over pyrrolide nitrogen. However, the slightly elongated Mg–N distance of 2.274(2) Å between the imine nitrogen and magnesium ion results from the lesser electron density over imine nitrogen atom. Nevertheless, both Mg–N distances are in agreement with reported values.[48]

Hydroboration of carbonyl compounds. After the successful synthesis of alkali and alkaline earth metal complexes **1**–**5**, we

employed them as catalysts for the hydroboration of un-activated carbonyl compounds. The present study also allows us to compare the catalytic activity of a number of transition metal complexes and main group metal complexes already known to effect the reduction of carbonyl compounds under benign conditions. To investigate the catalytic efficiency of complexes **1**–**5**, we screened the elementary reaction using *p*-methoxy benzaldehyde and pinacolborane (HBpin) with 3 mol% of the catalyst being loaded in neat condition at ambient temperature. The hydroboration reaction proceeded rapidly to produce *p*-OMeC$_6$H$_4$CH$_2$OBpin within 30 minutes when complexes **1** and **2** were used as catalysts (Table 1, entries 1–2). When complex **3** was used as the catalyst (Table 1, entry 3, FS 18–20 in ESI), complete conversion was achieved within 20 minutes. In contrast, the use of Ae metal complexes **4** and **5** exhibited sluggish activity towards catalytic hydroboration of *p*-methoxy benzaldehyde. Additionally, the reaction proceeded smoothly in organic solvents such as THF, toluene, benzene and hexane (Table 1, entries 6–9).



Scheme 3. Hydroboration of carbonyl compounds catalysed by complexes **1**–**5**.

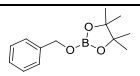
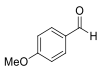
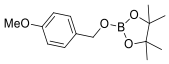
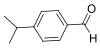
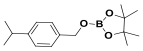
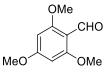
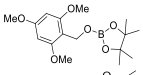
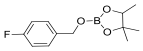
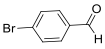
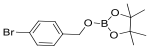
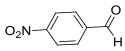
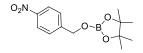
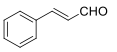
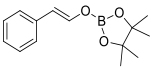
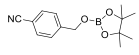
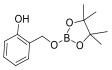
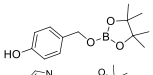
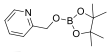
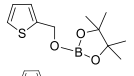
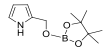
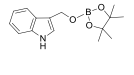
Table 1. Screening of the complexes **1**–**5** as catalysts for hydroboration of carbonyl compounds.

Entry	Substrate	Cat (3 mol%)	Time (Min)	Solvent	Conv (%)
1	p-OMePhCHO	**1**	30	Neat	99
2	p-OMePhCHO	**2**	30	Neat	99
3	p-OMePhCHO	**3**	20	Neat	99
4	p-OMePhCHO	**4**	30	Neat	50
5	p-OMePhCHO	**5**	30	Neat	50
6	p-OMePhCHO	**3**	30	THF	96
7	p-OMePhCHO	**3**	30	Toluene	98
8	p-OMePhCHO	**3**	30	Hexane	90
9	p-OMePhCHO	**3**	30	Benzene	98

Reaction conditions: catalysts **1–5** (0.03 mmol), *p*-methoxy benzaldehyde (1 mmol) with pinacolborane (1 mmol).

To explore the scope of the reaction, a range of aryl aldehydes were subjected to hydroboration with pinacolborane using potassium complex **3** (3 mol %). The results are outlined in Table 2. Aromatic aldehydes with one or more electron-releasing groups required one hour to yield 90–99% conversion at room temperature (Table 2, entries 2–4, FS 18–26 in ESI). Substrates with electron-withdrawing functional groups (F, Br, NO_2) underwent smooth hydroboration reactions to afford the corresponding borate ester within one hour (Table 2, entries 5–7, FS 27–35 in ESI). Cinnamaldehyde could also be converted to 2-(cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with a yield of 94%, indicating that the catalyst selectively reduced the carbonyl moiety over the double bond (C=C) present in the cinnamaldehyde (Table 2, entry 8, FS 36–38 in ESI). Aldehydes with heterocycles reacted rapidly with HBpin to give the desired borate ester product in high yield within one hour (Table 2, entries 12–15). To assess the functional group tolerance with respect to catalyst **3**, we chose the aldehydes with OH, NH_2, NH and CN as substrates. To our delight, 2-hydroxy benzaldehyde or 4-hydroxy benzaldehyde could be selectively converted to the corresponding borate esters by reducing carbonyl functionality, leaving behind only the dehydroocupling of hydroxyl with HBpin (Table 2, entries 10–11, FS 42–47 in ESI).[50] Similarly, when pyrrol 2-carboxaldehyde was reacted with HBpin in the presence of catalyst **3**, a chemoselective product PyCH$_2$OBpin was obtained, leaving the NH moiety unaffected (Table 2, entries 14, FS 54–56 in ESI). Analogously, corresponding chemoselective carbonyl reduced products were isolated by the reaction of indole 3 carboxaldehyde, 2,5 pyrrole dicarboxaldehyde with HBpin, using complex **3** as the catalyst (Table 2, entry 15–16, FS 57–62 in ESI). The reaction of ferrocenecarboxaldehyde (as aldehyde source) with HBpin also yielded the corresponding borate ester without affecting the ferrocene ring (Table 2, entry 17, FS 63–65 in ESI).

Table 2. Substrate scope for the hydroboration of carbonyl compounds catalysed by catalyst **3**.

S. No.	Substrate	Product	Time (h)	Yield (%)
1			<0.5	99
2			<0.5	95
3			1	92
4 [b]			1	90
5			1	95
6			1	95
7 [b]			1	93
8			1	94
9			1	94
10 [b]			1	85
11 [b]			1	90
12 [b]			1	93
13			1	95
14 [b]			1	93
15 [b]			1	92

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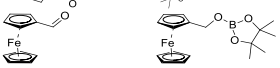
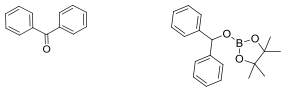
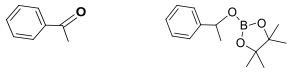
17[a]		1	95
18[a,b]		4	91
19[a]		3	95
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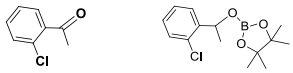
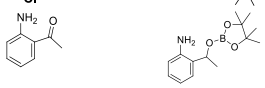
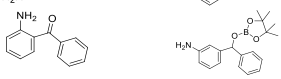
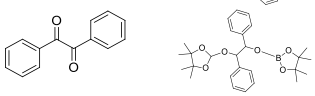
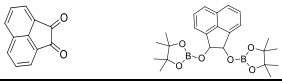
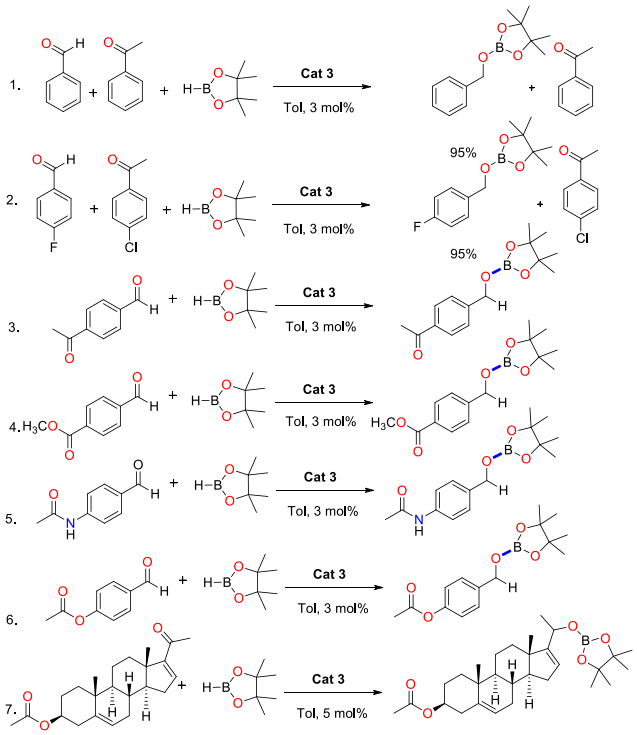
21[a,b]		3	93
22[a,b]		3	95
23[a]		3	95
24[a,b]		3	95
25[a,b]		3	85
26[a,b]		4	90
27[a,b]		4	93

Reaction conditions: catalyst **3** (3 mol%), [a] 5 mol% catalyst loading, reaction carried out at 30°C. [b] 0.5 ml toluene used as a solvent. Yields are determined by using ^{1}H NMR (400 MHz) integration of a characteristic product signal present in the reaction mixtures.

We wanted to extend this protocol for hydroboration of ketones, and during our initial comparison between acetophenone and HBpin, we observed that while 60% conversion of substrate occurred in one hour, three hours were required for the near-quantitative conversion (93%) of acetophenone, indicating that ketone hydroboration was relatively slower than that of aldehydes (Table 2, entry 19). However, aromatic ketones could be converted to the corresponding borate ester through a longer reaction time (three–four hours). The aromatic ketones with electron-releasing as well as electron-withdrawing functional groups underwent smooth reaction with HBpin to yield the corresponding reduced products within four hours at ambient temperature (Table 2, entries 20–21). To test the tolerance of catalyst **3** (5 mol%), 2-amino-, 3-amino- and 4-aminoacetophenone or 2-amino benzophenone were reacted with HBpin to yield the corresponding chemoselective borate ester product. In each case, no formation of cross-dehydrocoupling product[50] between amine and borane substrates (Table 2, entries 22–25) was observed. However, the reaction with di-keto compounds, such as benzil or acenaphthoquinone, with two equivalents of HBpin was slightly sluggish, and required four hours in room temperature to afford the doubly hydroborated product in good yield (Table 2, entry 26–27, FS 90–95 in ESI). There was no evidence of the formation of the singly hydroborated product in either reaction.

Selective hydroboration of aldehydes over ketones and other functional groups present in the substrate is an important transformation in organic synthesis.[49] To investigate the catalyst selectivity between aldehydes and ketones, we subjected stoichiometric amounts of benzaldehyde and acetophenone to one equivalent of HBpin using catalyst loading of 3 mol% and observed 95% selectivity in aldehyde hydroboration (Scheme 5, entry 1, FS 94–96 in ESI). Analogous results were obtained when 4-fluoro benzaldehyde and 4-chlorobenzophenone were simultaneously reacted with HBpin in 1:1:1 molar ratio (Scheme 5, entry 2, FS 97–99 in ESI). The selectivity of the aldehyde over ketone could also be achieved through the intramolecular hydroboration reaction of 4-acetyl benzaldehyde with one equivalent HBpin in the presence of catalyst **3** to give 4-$CH_3COC_6H_4CH_2OBpin$ exclusively (Scheme 5, entry 3, FS105-107 in ESI). The reaction of N-(4-formylphenyl) acetamide and 4-formylphenyl acetate with HBpin yielded the corresponding mono-borate ester by selective reduction of the aldehyde functional group over the amido and ester groups (Scheme 5, entries 5–6, FS108–113 in ESI). The methodology was successfully utilised for the selective reduction of aldehyde over a number of potential reducing groups present in steroid molecule 16-dehydropregnolone acetate (Scheme 5, entries 7, FS 114–116 in ESI).



Scheme 5. Selective hydroboration of aldehydes over ketones catalysed by complex **3**.

Plausible mechanism. The traditional mechanism involves the formation of an active metal hydride which acts as the active catalyst for the hydroboration reaction for carbonyl compounds.[51–63] In contrast to this, recently, Sen *et al.* and Ma *et al.* reported the use of

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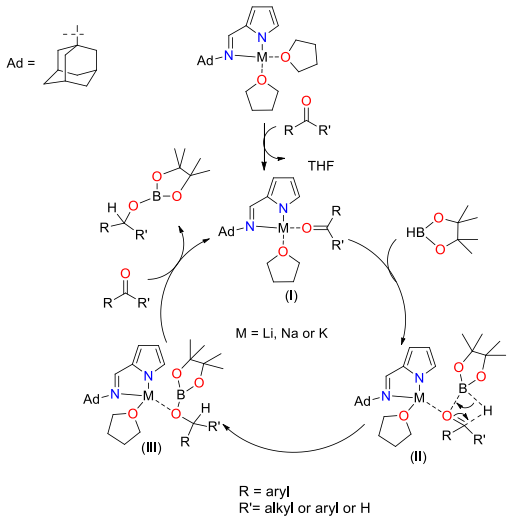
calcium iodide and ytterbium iodide complexes respectively as catalysts for the hydroboration of aldehydes as well as ketones, using the Lewis-acidic nature of metal towards the carbonyl compound, rather than formation of discrete metal hydride species. Thus, it is useful to elucidate on the mechanistic pathway of our process of hydroboration of aldehydes and ketones, as mediated by catalyst **3**. Based on the kinetic study, a plausible mechanism for the hydroboration of aldehyde and ketones is proposed in Scheme 4. In the first step of the proposed mechanism, the alkali metal ion of complex **3** polarises the carbonyl oxygen moiety to give an active catalytic species **I**, which is well known in literature.[64] In the next step, a nucleophilic attack occurs on the electron-deficient carbonyl carbon atom by the incoming hydride, leading to the formation of the four-membered transition state (**II**), which undergoes σ bond metathesis to give another intermediate **III**. In the final step, **III** reacts further with another molecule of ketone to give the hydroborate product RR'CHOBpin under immediate regeneration of active species **I**.



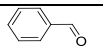
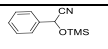
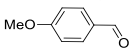
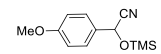
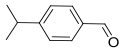
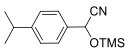
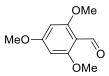
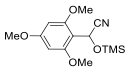
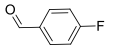
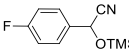
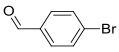
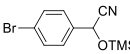
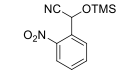
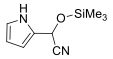
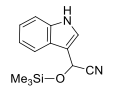
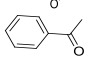
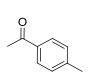
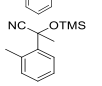
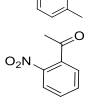
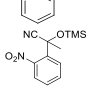
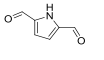
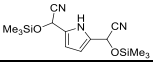
Scheme 4. Proposed catalytic cycle for hydroboration of carbonyl compounds catalysed by alkali metal complexes **1**–**3**.

For greater insight into the mechanism of the reaction, we carried out two control reactions of excess 2-methoxy-benzaldehyde and pinacolborane with catalyst **3** separately, and observed no significant changes under similar reaction conditions (FS 117–119), indicating that catalyst **3** is quite stable in the presence of the two substrates. To eliminate the possibility of the formation of KH as the active species by the reaction of alkali metal complex **3** and HBpin, we performed the catalytic hydroboration reaction between 2-hydroxy-benzaldehyde and HBpin by using KH or $KN(SiMe_3)_2$ under similar reaction conditions. In both cases, we observed the formation of cross dehydrocoupled (CDC) product C_6H_4CHO-2-OBpin as the sole product (FS 165 in ESI), indicating no presence of KH or $KN(SiMe_3)_2$ in the catalytic hydroboration of carbonyl compounds as proposed in Scheme 4.

Cyanosilylation of carbonyl compounds.

In literature a wide range of catalyst have been reported including alkali metal fluorides for cyano sillylation of carbonyl compounds. [65-69] After screening the efficiency of catalyst **3** for the hydroboration reaction, we were interested in probing our catalyst further by addition of trimethylsilyl cyanide to the carbonyl compounds to produce corresponding cyanohydrins. The initial reaction was performed using one equivalent of benzaldehyde with one equivalent of TMSCN in the presence of 3 mol% of catalyst **3**. We observed that quantitative conversion was accomplished within 30 minutes (Table 3, entry 1, FS 120–121 in ESI). Additionally, the use of various solvents did not impede this reaction. Moreover, to explore the substrate scope, we conducted the same reaction using a number of carbonyl compounds with electron-donating and electron-withdrawing functional groups. Catalyst **3** exhibited excellent tolerance towards these functionalities and yielded 80–95% of the product (Table 3, entries 2–7, FS 122–133 in ESI) under optimum conditions. Not surprisingly, the cyanosilylation reaction of ketones took slightly longer to yield near-quantitative conversion (1–1.5 hours, Table 3, entries 10–12, FS 138–143 in ESI). Moreover, the reaction of 2-pyrrole carboxaldehyde, indole 3-carboxaldehyde, and 2,5 pyrrol dicarboxaldehyde with TMSCN led to the chemoselective cyanosilylation of carbonyl moiety, leaving behind a free amine NH group in each case (Table 3, entries 8, 9 and 13, FS 134–137 and143–144 in ESI).

Table 3. Substrate scope for the cyanosilylation of carbonyl compounds catalysed by catalyst **3**.

S. No.	Substrate	Product	Time	Yield
1			30	99
2			30	99
3			30	99
4 [a]			45	99
5			30	99
6			40	99
7 [a]			45	99
8			50	99
9 [a]			60	99
10			60	99
11			70	99
12 [a]			90	99
13[a]			80	99

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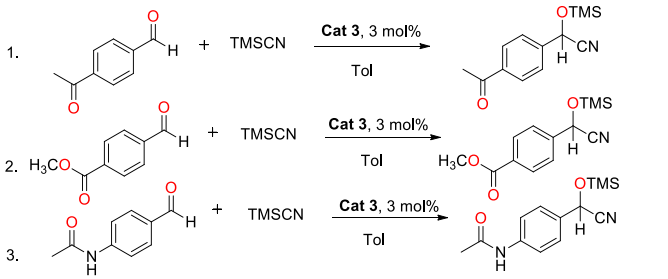
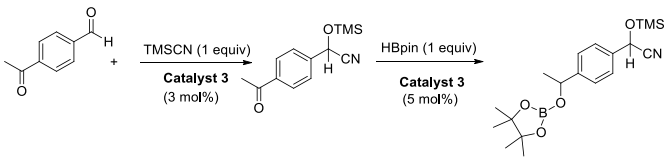
Reaction conditions: Catalyst **3** (3 mol%), reaction carried out at 30°C [a] 0.5 ml toluene used as a solvent and yields were determined by using ^{1}H NMR spectroscopy.



Scheme 6. Selective cyanosilylation of aldehydes over ketones catalysed by complex **3**.

To investigate the selectivity of catalyst **3**, we performed a reaction with 4-acetyl benzaldehyde with one equivalent of TMSCN in the presence of 3 mol% of catalyst and we obtained a 95% yield of 4-acetylphenyl-2-((trimethylsilyl)oxy acetonitrile, indicating that the aldehyde group was selected over the ketone group for cyanosilylation (Scheme 6, entry 1, FS 146–147 in ESI). Analogous results were observed when 4-formyl benzoate, N-(4-formyl-phenyl)acetamide and 4-formyl phenylacetate was reacted with TMSCN to yield the corresponding cyanohydrin by selective reduction of the aldehyde functional group over the amido and ester groups (Scheme 6, entries 2-3, FS 148–151 in ESI).

Sequential cyanosilylation-hydroboration of 4 acetyl benzaldehyde. Sequential cyanosilylation-hydroboration of dicarbonyls was examined, using one equivalent of 4-acetyl benzaldehyde with 1 equivalent of TMSCN in the presence of 3 mol% of catalyst **3** to yield the corresponding cyanohydrin product by selective reaction of the aldehyde group at room temperature. Moreover, the addition of one equivalent of HBpin and 5 mol% of catalyst **3** to the cyanohydrin caused the reaction of the ketone with HBpin at 30°C and conversion to cyanohydrin borate ester (FS 152–154 in ESI). However, a mixture of products was obtained when other dialdehydes and diketones were used as substrates under similar conditions.



Scheme 7. Sequential cyanosilylation/hydroboration of 4-acetyl benzaldehyde catalysed by complex **3**.

Conclusions

We have successfully synthesised alkali (Li, Na, K) and alkaline earth metal (Mg and Ca) complexes supported by *N*-adamantyl-iminipyrrolyl ligand and established their molecular structures. Potassium complex **3** has proved its competence as a catalyst for the catalytic hydroboration of a wide range of aldehydes and ketones, thus manifesting its versatility as a pre-catalyst for this reaction. Complex **3** has also exhibited unusual tolerance towards active functional groups such as -NH, -OH, -S, -CN, -OMe, -F, -Cl, etc. at ambient temperature. Further, complex **3** is an active catalyst for the cyanosilylation reaction of carbonyl compounds. The proposed mechanism, based on controlled reactions, suggests the possible formation of a Lewis acid-base adduct by the metal ion and carbonyl compound as the transition state, excluding the formation of metal hydride. The kinetic studies suggest that the hydroboration reactions displayed first-order kinetics with respect to the catalyst **3**.

Experimental

General considerations.

All manipulations of air-sensitive materials were performed under inert atmosphere in flame-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} Torr) or in an argon-filled M. Braun glovebox. ^{1}H NMR (400 MHz), ^{11}B NMR (128.4 MHz) and ^{13}C{^{1}H} (100 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. Pyrrole-2-carboxaldehyde, adamantylamine, aldehydes and ketones and trimethylsilyl cyanide, $KN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $LiN(SiMe_3)_2$, MgI_2 were purchased from Sigma Aldrich. Amines were distilled over CaH_2 prior to use. NMR solvent ($CDCl_3$ and C_6D_6) was purchased from Sigma Aldrich and C_6D_6 was dried over Na/K alloy.

Synthesis of [2-(AdN=CH)C$_4$H$_3$NH] (L–H). To an ethanol solution (15 mL) of pyrrole-2-carboxaldehyde (2.0 g, 21.0 mmol), ethanol solution of adamantylamine (3.2 g, 21.0 mmol), was added while stirring. The reaction was stirred for another eight hours at room temperature. The solution was evaporated under reduced pressure to obtain a colourless solid. The compound was re-crystallised in hot ethanol to give colourless crystals.
Yield: 4.5 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.50 (b, 1H, NH), 8.17 (s, 1H, N=C-H), 6.82 (s, 1H, Py-*H*), 6.51 - 6.49 (m, 1H, Py-*H*), 6.24 - 6.23 (m, 1H, Py-*H*), 2.04 (m, 3H, Ad-H), 1.81 - 1.69(m, 12H, Ad-H) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 146.4 (PyC=N), 131.2 (Py-C), 121.3 (Py-C), 113.5 (Py-C), 109.3 (PyC), 56.9 (Ad-C), 43.3 (Ad-C), 36.6 (Ad-C), 29.6 (Ad-C) ppm. ($C_{15}H_{20}N_2$) (228.3). Calc. C 78.90, H 8.83, N 12.27; found C 78.27 H 8.56, N 11.79.

Synthesis of [{2-(AdN=CH)C$_4$H$_3$NLi(THF)}$_2$] (1). In a 10 mL sample vial, 50 mg (0.219 mmol) of **L–H** and 37 mg of $[LiN(SiMe_3)_2]$ (0.219 mmol) were mixed together with 5 mL of THF. After six hours of stirring at room temperature, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added to it and kept at −35°C. Colourless crystals of complex **2** were obtained after two days.
Yield: 60 mg (89%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 8.26 (s, 2H, N=C-H), 7.57 (b, 2H, Py-*H*), 7.05-7.04 (m, 2H, Py-*H*), 6.83 (b, 2H, Py-*H*), 3.44 (m, THF), 2.02 (m, 7H, Ad-H), 1.73 - 1.60(m, 10H, Ad-H), 1.43 - 1.40 (m, THF), 1.29 (m, 12, Ad-H) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 151.6 (PyC=N), 138.4 (Py-C), 131.8 (Py-C), 115.0 (Py-C), 108.1 (PyC), 65.3 (THF), 52.6 (Ad-C), 41.4 (Ad-C), 34.3 (Ad-C), 27.5 (Ad-C) 22.8(THF) ppm. ($C_{38}H_{54}Li_2N_4O_2$) (612.7). Calc. C 74.49, H 8.88, N 9.14; found C 73.85 H 8.55, N 8.69.

Synthesis of [{2-(AdN=CH)-C_4H_3N}Na$(THF)_2$}$_2$] (2). In a 10 mL sample vial, 50 mg (0.219 mmol) of **L–H** and 40.7 mg (0.219 mmol) of [NaN$(SiMe_3)_2$] were mixed together with 5 mL of THF. After six hours of stirring, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added to it and kept at −35°C. Colourless crystals of complex **2** were obtained after two days.
Yield: 75 mg (92%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.95 (s, 2H, N=C-H), 6.46-6.45 (m, 2H, Py-*H*), 6.33 - 6.32 (m, 2H, Py-*H*), 6.24 - 6.22 (m, 2H, Py-*H*), 3.59 - 3.55 (m, THF), 2.03 (m, 6H, Ad-H), 1.76 - 1.76 (m, 12H, Ad-H), 1.66 - 1.61 (m, 12H, Ad-H), 1.43 - 1.40 (m, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 151.6 (PyC=N), 138.4 (Py-C), 131.8 (Py-C), 115.0 (Py-C), 108.1 (PyC), 65.3 (THF), 52.6 (Ad-C), 41.4 (Ad-C), 34.3 (Ad-C), 27.5 (Ad-C) 22.8 (THF) ppm. ($C_{42}H_{62}Na_2N_4O_3$) (716.9). Calc. C 70.36, H 8.72, N 7.81; found C 69.68 H 8.31, N 7.41.

Synthesis of [{2-(AdN=CH)C_4H_3NK(THF)}$_n$] (3). In a 10 mL sample vial, one equivalent (50 mg, 0.219 mmol) of **L1** and one equivalent of [KN$(SiMe_3)_2$] (43.8 mg, 0.219 mmol) were mixed together with 5 mL of THF. After six hours, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added to it and kept at −35°C. Colourless crystals of complex **3** were obtained after two days.
Yield: 70 mg (91%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 8.16 (s, 1H, N=C-H), 7.49 (m, 1H, Py-*H*), 6.96-6.95 (m, 1H, Py-*H*), 6.75 (m, 1H, Py-*H*), 3.34-3.31 (m, THF), 1.92 (m, 3H, Ad-H), 1.63-1.62(m, 6H, Ad-H), 1.43-1.40 (m, THF), 1.20 - 1.17 (m, 6H, Ad-H) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 146.1 (PyC=N), 132.4 (Py-C), 114.4 (Py-C), 110.3 (PyC), 68.4 (THF), 57.5 (Ad-C), 44.2 (Ad-C), 37.4 (Ad-C), 30.6 (Ad-C), 26.3 (THF) ppm. ($C_{19}H_{27}KN_2O$) (338.5). Calc. C 67.41, H 8.04, N 8.28; found C 66.59 H 7.71, N 7.65.

Synthesis of [κ^2-{2-(AdN=CH)-C_4H_3N}$_2$Ae$(THF)_2$] [Ae = Mg (4), Ca (5)]. Inside the glove box, in a 25 mL pre-dried Schlenk flask, compound **L–H** (50 mg, 0.219 mmol) was mixed with 44 mg of [KN$(SiMe_3)_2$] and 31 mg MgI_2 (0.1095 mmol) or 32 mg CaI_2 (0.1095 mmol) in 10 mL THF solvent at ambient temperature and the reaction mixture was stirred for eight hours. The white precipitate of KI was filtered, and the filtrate was evaporated under reduced pressure. The resulting white residue was purified further by washing with pentane and was re-crystallised from a mixture of THF–pentane (1:2 ratio) at −35°C.
4: Yield: 130 mg (92%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 8.03 (s, 2H, N=C-H), 6.49 (m, 4H, Py-*H*), 6.26-6.24 (m, 2H, Py-*H*), 3.59-3.55 (m, THF), 2.00 (m, 6H, Ad-H), 1.76-1.55(m, 24H, Ad-H), 1.43-1.40 (m, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 146.8 (PyC=N), 132.4 (Py-C), 114.4 (Py-C), 110.3 (Py-C), 68.4 (THF), 57.5 (Ad-C), 44.2 (Ad-C), 37.4 (Ad-C), 30.7 (Ad-C) 26.5 (THF) ppm. ($C_{46}H_{70}MgN_4O_4$) (767.3). Calc. C 72.00, H 9.19, N 7.30; found C 69.29 H 8.76, N 6.87.
5: Yield: 135 mg (93%). ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.98 (s, 2H, N=C-H), 6.47 (m, 2H, Py-*H*), 6.35 (m, 2H, Py-*H*), 6.25-6.24 (m,2H, py-H), 3.59-3.55 (m, THF), 1.93 (m, 8H, Ad-H), 1.47-1.43(m, 3H), Ad-H), 1.42-1.36 (m, 12H, Ad-H) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ_C 145.4 (PyC=N), 128.5 (Py-C), 120.8 (PyC), 113.4 (Py-C), 109.6 (Py-C), 67.7 (THF), 55.6 (Ad-C), 46.5 (Ad-C), 36.5 (Ad-C), 29.6 (Ad-C) 25.6 (THF) ppm. ($C_{46}H_{70}CaN_4O_4$) (783.1). Calc. C 70.55, H 9.01, N 7.15; found C 69.72 H 8.27, N 6.55.

Typical procedure for hydroboration of carbonyl compounds:

Hydroboration of aldehydes or ketones was carried out using the following standard protocol. In the glove box, the chosen pre-catalyst (0.03–0.05 mmol) was loaded into a Schlenk tube, and subsequently, HBpin (pinacolborane) (1 mmol) followed by aldehyde or ketone (1 mmol) was added. The reaction was stirred in an oil bath at the desired temperature (30°C). Substrate conversion was monitored by examination of the ^{1}H NMR, which indicated the formation of a new CH_2 peak for aldehydes and CH peak for ketones.

Typical procedure for TMSCN addition to carbonyl compounds:

TMSCN addition of carbonyl compounds was carried out using the following standard protocol. In the glove box, the chosen pre-catalyst (0.03 mmol) was loaded into a Schlenk tube, and subsequently, TMSCN (1 mmol) followed by aldehyde or ketone (1 mmol) was added. The reaction was stirred in an oil bath at the desired temperature (30°C).

Conflicts of interest

There are no conflicts to declare.

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Alkali Metal Complexes as Efficient Catalysts for Hydroboration and Cyanosilylation of Carbonyl Compounds

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Graphical Abstract

Catalytic hydroboration of aldehydes and ketones with pinacolborane (HBpin) and catalytic cyanosilylation of carbonyl compounds with trimethylsilyl cyanide using alkali metal (Li, Na, K) complexes as precatalyst under mild conditions are reported.