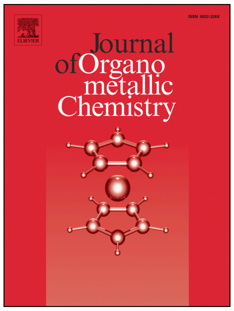

Efficient and selective carbonyl hydroboration catalyzed by a lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$]

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Efficient and selective carbonyl hydroboration catalyzed by a lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$]

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Abstract: The well-defined lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$] **2** based on a bis(imino)aryl ligand has been successfully prepared, crystallographic characterized and employed as an efficient catalyst for hydroboration of a wide range of aldehydes and ketones with pinacolborane (HBpin) at room temperature. Both aldehyde and ketone hydroboration proceeded efficiently (>99% conversion in <15 min) and could be directly carried out in a CDCl$_3$ solution. In addition, chemoselective hydroboration of aldehydes over ketones was also achieved under these conditions.

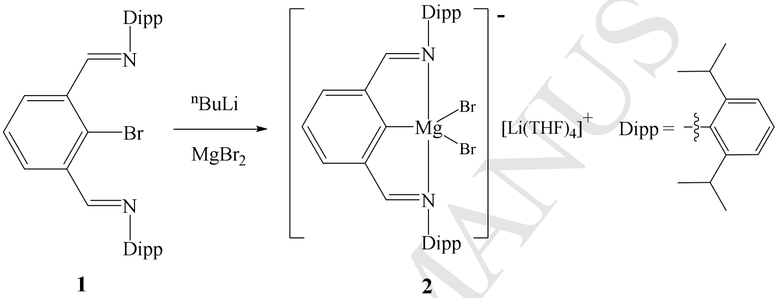
Keywords: Mg-Li complex; Hydroboration; Aldehyde; Ketone

1. Introduction

The transformations of organic unsaturated substrates play an important role in organic synthesis since the resultant products are a class of versatile synthetic intermediates [1]. Catalytic hydroboration of carbonyl compounds with pinacolborane (HBpin) was one of these key transformations. The formed borate ester intermediates could be further employed for the commodity and materials synthesis etc, on the other hand, it was also easily converted into the corresponding alcohols [2-3]. Metal borohydrides such as NaBH$_4$ have been commonly used for hydroboration, however, they frequently show poor functional-group tolerance. The catalytic hydroboration of carbonyl compounds has been extensively studied by many research groups using transition metal [4], main group compound [5-19], and even rare-earth metal catalysts respectively [20-22]. The bimetallic complexes generally have a synergistic effect on catalysis [23]. We have found that the catalytic activity of the sterically bulky Schiff-base Mg-Na bimetallic ionic complex is superior to the corresponding neutral monometallic magnesium complexes in the similar hydrosilylation of ketones with (EtO)$_3$SiH recently [24]. To our surprise, compared to the mono-metal catalysts, no bimetal catalyzed hydroboration of carbonyl compounds has been reported hitherto. Herein we report the synthesis and crystallographic characterization of a lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$] **2** and its application in the hydroboration of aldehydes and ketones which displayed a good operational convenience and high efficiency.

2. Results and discussion

As depicted in **Scheme 1**, the bis(imino)aryl NCN pincer ligand **1** was treated with one equiv. of ^{n}BuLi in THF to generate the corresponding lithium salt, then further reacted with equimolar amounts of $MgBr_2$. The complex **2** was obtained as colorless crystals in good yield. The crystal structure of complex **2** and selected bond lengths and angles are shown in **Figure 1**. The geometry of the magnesium atom in **2** is a distorted trigonal bipyramid with the two imine nitrogen atoms of the ligand in the apical position and one carbon atom of the ligand and two bromine atoms in the equator which is almost identical to the ideal value of 360^{o}. The Mg atom in **2** is essentially coplanar with the NCN plane. The geometry of four-coordinated cationic lithium atom in **2** is slightly distorted tetrahedral, coordinated by four oxygen atoms from the coordinated THF molecules. The bond length of Mg–Br [2.4733 (14) Å, 2.4771(15) Å] in **2** is slightly shorter than that of the β-diketiminate Mg-Li bimetallic complex [25]. The bond angle of Br(1)–Mg(1)–Br(2) is 116.24(6)°.



1 **2**

Scheme 1. Synthesis of complex 2.

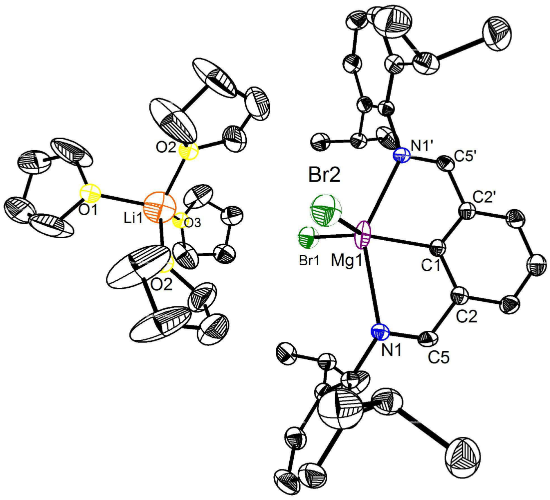
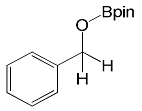
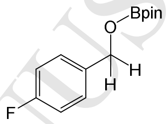
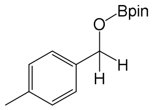
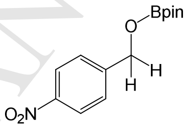
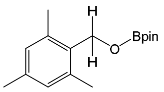
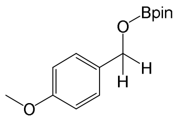
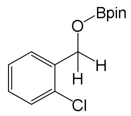
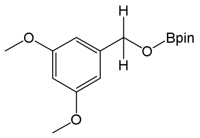
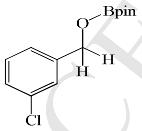
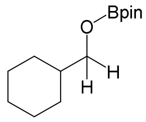
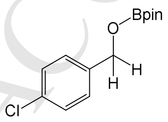
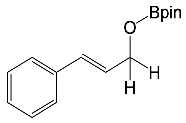
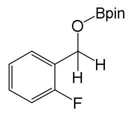
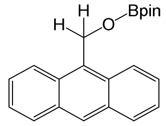
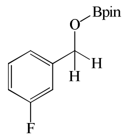
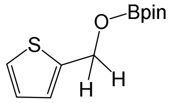


Figure 1. Molecular structure of **2** (50% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)–Br(1) 2.4733 (14), Mg(1)–Br(2) 2.4771(15), Mg(1)–N(1) 2.598(2), Mg(1)–C(1), 2.105(4), N(1)–C(5) 1.275(3), C(2)–C(5) 1.466(4), Br(1)–Mg(1)–Br(2) 116.24(6), C(1)–Mg(1)–Br(1) 121.50(11), C(1)–Mg(1)–Br(2) 122.25(11), Br(1)–Mg(1)–N(1) 98.98(5), Br(2)–Mg(1)–N(1) 99.95(6), N(1)–Mg(1)–N(1)′ 143.70(11).

In order to explore potential utility of the above NCN pincer ligand-based complex **2**, we investigated its application in the catalytic hydroboration of aldehydes and ketones. It was noted that the blank reaction between benzaldehyde and HBpin was observed to only afford less than 5% yield in the absence of the catalyst at room temperature after 15min [12]. However, the same reaction with 1 mol% catalyst loading of **2** gave a quantitative yield in C_6D_6 at room temperature within 15 min. Compared with the reported hydroboration of benzaldehyde catalyzed by the similar

Table 1. Hydroboration of aldehydes catalyzed by 2

Entry	Product	Time (min)	Yield (%)^a	Entry	Product	Time (min)	Yield (%)^a
1		15	99	9		15	99
2		15	99	10		15	99
3		15	99	11		15	99
4		15	92	12		15	99
5		15	99	13		15	99
6		15	99	14		15	99
7		15	99	15		15	99
8		15	99	16		15	99

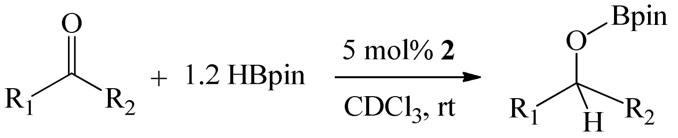
[a] The reaction was monitored by ^{1}H NMR spectroscopy.

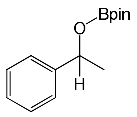
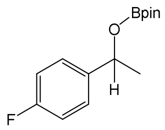
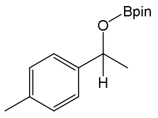
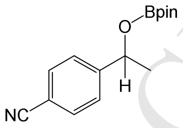
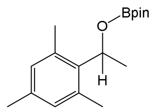
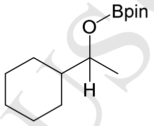
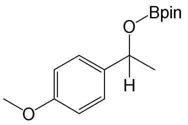
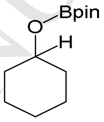
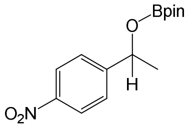
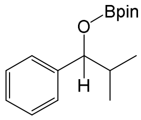
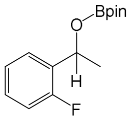
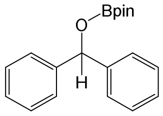
calcium iodide complex [9], the complex **2** showed a slightly higher activity (**Mg-Li**: 1 mol% catalyst, 15 min, 99% yield; *VS* **Ca**: 2 mol%, 40 min, 90-99% yield). To our surprise, the same reaction could be also carried out in a $CDCl_3$ solution and gave the same high yield (**Table 1**, entry 1). This is quite different from the previously reported metal catalyzed aldehyde hydroboration which is strictly performed in purified C_6D_6 solution in general. The reason could be that complex **2** is less air- and moisture-sensitive compared to other metal complexes, particularly for the similar magnesium alkyl or hydride complexes. Due to the very higher price of C_6D_6, we chose the cheaper $CDCl_3$ as solvent that directly used from commercial available and no further purified to expand the scope of aldehydes hydroboration.

Generally, the hydroboration of various aldehydes with 1 mol% catalyst loading of **2** could be completed within 15 min at room temperature in quantitative conversion. For example, the hydroboration of a series of benzaldehyde derivatives with electron-donating and electron-withdrawing groups such as -Me, -Cl, -F, -NO_2 and -OMe all afforded the corresponding alkoxypinacolboronate esters in 99% yields (**Table 1**, entries 2, 3, 5-12) except for the ortho-chloro substituted benzaldehyde gave 92% yield (**Table 1**, entry 4). Furthermore, cyclohexylaldehyde, α, β-unsaturated cinnamaldehyde, heterocyclic aldehyde 2-thiophenecarboxaldehyde, and even 9-anthraldehyde were also hydroborated in full conversion within 15 min (**Table 1**, entries 13-16).

Encouraged by the above aldehyde hydroboration results, we then examined the hydroboration of a wide range of ketones. As expected, the hydroboration of more sterically bulky ketonic carbonyl functions catalyzed by Mg-Li bimetallic complex **2** required slightly higher catalyst loading than that of aldehydes to achieve high yields. The initial investigation on the hydroboration of acetophenone with 1 mol% catalyst loading of **2** only afford 80% yield in $CDCl_3$ within 15 min, however, increasing the amount of catalyst to 5 mol%, 99% yield of product was obtained in the same time (**Table 2**, entry 1). Compared with the similar reported calcium iodide catalyst, Mg-Li bimetallic catalyst showed slightly higher efficiency (**Mg-Li**: 5 mol% catalyst, 15min, 99% yield *VS* **Ca**: 3 mol% catalyst, 5h, 95% yield) [9]. In most cases, the ketone hydroboration reaction was completed within 15 min in quantitative yield. The hydroboration of acetophenone substrates with electron-donating or electron-withdrawing group such as -Me, -OMe, -NO_2, and -F all produced the corresponding borate ethers in 99% yield (**Table 2**, entries 2, 4-7). The reaction of 4-acetylbenzonitrile required a slightly longer time (30 min) to get 99% yield (**Table 2**, entry 8). Under the same reaction condition, for the 2,4,6-trimethylacetophenone, only 80% conversion was observed in 15 min (**Table 2**, entry 3). This once again highlighted the importance of steric factors in the hydroboration reactions. The hydroboration of dialkyl ketones also finished with full yield in a very short time (**Table 2**, entries 9, 10). Changing methyl moiety of acetophenone to isopropyl or phenyl substituent, the quantitative yield was obtained in 15 min as well (**Table 2**, entries 11, 12). The results of ketone hydroboration indicated that Mg-Li bromide complex **2** was more reactive than the closely related calcium iodide complex (73-95%) [9].

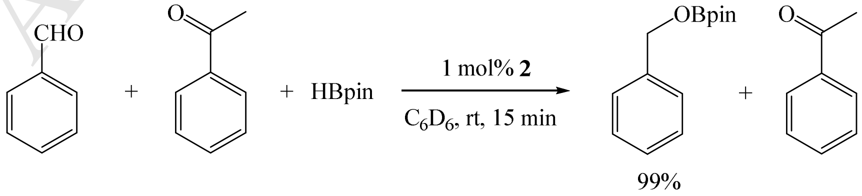
Table 2. Hydroboration of ketones catalyzed by 2



Entry	Product	Time (min)	Yield (%)^{a}	Entry	Product	Time (min)	Yield (%)^{a}
1		15	99	7		15	99
2		15	99	8		30	99
3		15	80	9		15	99
4		15	99	10		15	99
5		15	99	11		15	99
6		15	99	12		15	99

^{a} The reaction was monitored by ^{1}H NMR spectroscopy.

In addition, we also examined the chemoselectivity of hydroboration of aldehyde and ketone. The mixture solution of benzaldehyde (1 equiv.), acetophenone (1 equiv.) and HBpin (1 equiv.) was treated with 1 mol% complex **2** at room temperature. The benzaldehyde was completely converted into the corresponding borate ether in 15 min, however, acetophenone remained almost intact. This is similar to the previous reports of other metal catalysts [9, 20-22].



Scheme 2. Chemoselective hydroboration of aldehyde/ketone catalyzed by 2.

3. Conclusions

In summary, we have successfully synthesized a lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$] **2**. The catalytic investigation revealed that it could be employed as an efficient and chemoseletive catalyst for the hydroboration of aldehydes and ketones with HBpin at room temperature in a relative cheaper CDCl$_3$ solution. To the best of our knowledge, this is the first example of Mg-Li bimetallic complex catalyzed hydroboration of aldehydes and ketones. This protocol provided another operational convenience and efficient method for catalytic hydroboration of carbonyl compounds.

4. Experimental Section

All air-sensitive compounds were carried out using standard Schlenk-line or glovebox techniques under high-purity argon. Diethyl ether, toluene, THF and hexane were dried and distilled from molten sodium. ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra were recorded at 25 °C with a Bruker Avance III 600 MHz spectrometer and were referenced to the resonances of the solvent used. Elemental analysis was performed by the Elemental Analysis Laboratory of the Advanced Analysis and Testing Center at Nanjing Forestry University. Melting points were determined with an INESA-WRR apparatus and are uncorrected. Ligand **1** was prepared according to literature procedure [26]. CDCl$_3$ (99.8%) and HBpin (97.0%) were from CIL and TCI respectively and no further purified. Other reagents were used as received.

Synthesis of complex 2

^{n}BuLi (1.8 mL, 2.5 M in hexane, 4.50 mmol) was added dropwise to a THF (30 mL) solution of ligand **1** (2.30 g, 4.33 mmol) at -78°C and was stirred for 1 h. The reaction solution was warmed to -40 °C to stir for another 2 h and then was added to a THF suspension (20 mL) of MgBr$_2$ (0.82 g, 4.45 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 days. The yellow solution was concentrated to ca. 10 mL to afford a large amount of crystals and the supernatant solution was concentrated again to afford a second crop of complex **2** (Yield 2.71 g, 67%). m.p 223-225 °C, ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 8.29 (s, 2 H, C*H*=N), 7.32-7.05 (m, 9 H, Ar-*H*), 3.53 (m, 20 H, C*H*(CH$_3$)$_2$+C*H*$_2$O of THF overlap), 1.33 (m, 16 H, C*H*$_2$ of THF), 1.19 (d, 24 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 171.2 (*C*H=N), 149.2, 144.1, 140.3, 137.7, 132.4, 127.1, 124.9, 123.2 (Ar-*C*), 68.3 (*C*H$_2$O), 25.6 (*C*H$_2$), 28.3 (*C*H(CH$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$). Anal Calcd for $C_{48}H_{71}Br_2LiMgN_2O_4$: C, 61.91; H, 7.69; N, 3.01. Found C, 62.25; H, 7.94; N, 2.87.

General procedure for catalytic hydroboration of aldehydes or ketones

In a glove box, catalyst **2** (aldehydes: 1 mol%, ketones: 5 mol%) was added to a solution of aldehydes or ketones (0.25 mmol) and HBpin (1.2 equiv.) at room temperature in a common NMR tube which was charged with CDCl$_3$ (0.4 mL). The progress of the reaction was monitored by ^{1}H NMR and ^{11}B NMR.

X-ray crystal structure determination

Crystallographic data for complex **2** is given in Table 3. Diffraction data was collected on a Bruker D8 VENTURE PHOTON 100 diffractometer using a graphite-monochromated MoKα radiation (0.71073Å) at 135 K in the ω-2θ scan mode. In all cases, an empirical absorption correction by SADABS was applied to the intensity data. The structure was solved by direct methods and refined on F2 by full-matrix least-squares methods using the SHELXTL crystallographic software package. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in calculated positions (riding model). CCDC 1830603 contains the supplementary crystallographic data for complex **2**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for complex **2**.

Formula	$C_{48}H_{71}Br_2LiMgN_2O_4$	Mr	931.12
Crystal system	orthorhombic	Space group	Pnma
a (Å)	21.7324(9)	α (°)	90(4)
b (Å)	21.0958(10)	β (°)	90(4)
c (Å)	10.5148(5)	γ (°)	90(4)
V (A^3)	4820.6(4)	Z	4
D_{calc} (g cm^{-3})	1.283	T (K)	135(2)
μ (mm^{-1})	1.737	F (000)	1960
R_1 (obs data)	0.0498	wR_2 (obs data)	0.1041

Acknowledgements

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Highlights

1. A new well-defined lithium NCN-Pincer magnesiate complex [Li(THF)$_4$][NCN-MgBr$_2$] has been prepared.

2. The carbonyl hydroboration has been efficiently catalyzed by the Mg-Li complex.

3. Chemoselective hydroboration of aldehydes over ketones was observed.