ORGANOMETALLICS

pubs.acs.org/Organometallics Article

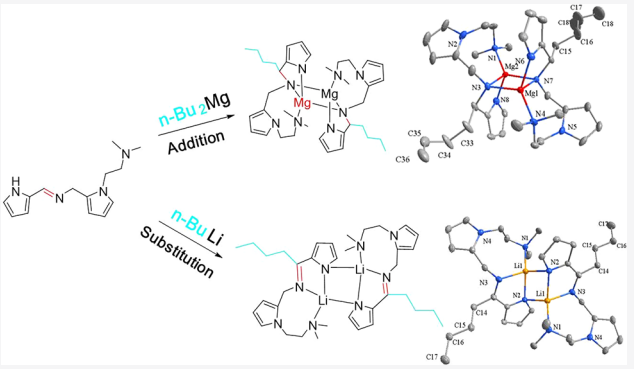
Nucleophilic Addition and α-C−H Substitution Reactions of an Imine Mediated by Dibutylmagnesium and Organolithium Reagents

Yan Dang,[§] Yalan Wang,[§] Yafei Li, Man Xu, Chaohong Jia, Yanhua Lu, Liang Zhang, Yahong Li,* and Yuanzhi Xia*

Cite This: *Organometallics* 2021, 40, 1830−1837 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A series of nucleophilic addition reactions and α-C−H substitution reactions of an imine-containing ligand 2-(2-((((1*H*-pyrrol-2-yl)methylene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine (HL1) were reported. The reactions of HL1 with 0.5 and 2 equiv of $^{n}Bu_2Mg$, respectively, gave two complexes of compositions $[Mg(L1)_2]$ (**1**) and $[Mg_2(L2)_2]$ (**2**) (H_2L2 = *N*-((1-(2-(dimethylamino)ethyl)-1*H*-pyrrol-2-yl)methyl)-1-(1*H*-pyrrol-2-yl)pentan-1-amine). The nucleophilic addition of $^{n}Bu_2Mg$ to the C═N bond of the HL1 ligand occurred in the process for the formation of **2**. Treatment of HL1 with 2 and 1 equiv of ^{n}BuLi generated $[Li_2(L3)_2]$ (**3**) (HL3 = 2-(2-(((1-(1*H*-pyrrol-2-yl)-pentylidene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine) and $[Li_2(L1)_2]$ (**4**). An α-C−H substitution of the HC═NR moiety of the HL1 ligand triggered by ^{n}BuLi was discovered in the preparation of **3**. The formation of **3** demonstrates a new concept for the C−C coupling that involved inert C−H bond activation of HC═NR skeleton. The reactions of HL1 with MeLi, *sec*-BuLi, and tert-BuLi, respectively, were also examined. The products for both the nucleophilic addition of organolithium reagents to the C═N bond and α-C−H substitution of the HC═NR moiety of the HL1 ligand were determined. The mechanisms for the formations of **2** and **3** were rationalized by DFT calculations. The hydroboration reactions catalyzed by **2** were investigated, and these reactions characterize ample substrate scope, very good yields, and high selectivity.



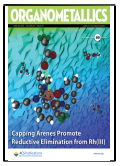
INTRODUCTION

Imines, due to the reactivity of the C═N bond, are valuable building blocks for the synthesis of various compounds with fundamental important functionalities. Molecules with the C═N bond are utilized as the ligands for the coordination complexes[1] and applied as key intermediates in the preparation of pharmaceutical-based compounds.[2] Particularly, imines have enjoyed an outstanding place in the synthesis of amine scaffolds, owing to the prevalence of amines as feedstock chemicals, building blocks for biologically active compounds, and valuable species in the agrochemical and polymer industries.[3] Consequently, the rapid and efficient synthesis of amines from imines is an energetically pursued area.

Several methodologies are developed for these transformations.[4] The important strategies include: (i) photocatalytic alkylation of imines enabled by organic photocatalysts[5] or metal catalysts;[6] (ii) nucleophilic additions of the C═N bond of imines by dialkylzinc,[7] Grignard reagents,[8] and organolithium complexes.[9] Several review articles have been published on this topic.[10] Reports of Hevia[11] and Capriati[12] have demonstrated that the additions of organolithium reagents to imines are efficient and sustainable approaches to amines, generating target amines in deep eutectic solvents and water. In contrast to the facile nucleophilic additions of organolithium reagents to imines, the additions to imines by dialkylmagnesium reagents are less common.[13] It was found that the dialkylmagnesium reagents could only be added to the activated C═N bonds.[13a] Recent work of Capriati and co-workers showed that the addition of organomagnesium reagents to imines is a facile protocol to produce amine compounds.[13b] Owing to the commercial availability and cheapness of dialkylmagnesium reagents, the preparation of amines by the addition of organomagnesium reagents to unactivated C═N bond is of practical importance.

We have prepared and structurally characterized two magnesium complexes $[Mg(L1)_2]$ (**1**) and $[Mg_2(L2)_2]$ (**2**) (HL1 = 2-(2-((((1*H*-pyrrol-2-yl)methylene)amino)methyl)-

Received: December 30, 2020
Published: June 18, 2021



https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine; H_2L2 = *N*-((1-(2-(dimethylamino)ethyl)-1*H*-pyrrol-2-yl)methyl)-1-(1*H*-pyrrol-2-yl)pentan-1-amine). Two lithium compounds $[Li_2(L3)_2]$ (**3**) (HL3 = 2-(2-(((1-(1*H*-pyrrol-2-yl)pentylidene)amino)-methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethyl-ethan-1-amine) and $[Li_2(L1)_2]$ (**4**) were also isolated. The α-C−H substitution of the HC═N unit of the HL1 ligand occurred in the process for preparing **3**. Due to the increased electrophilicity of azomethine carbon of imines compared with that of aldehydes,[7a] the α-C−H substitution of HC═N moiety of aldimines is a formidable challenge. As can be seen in Scheme 1, the atomic charge of the azomethine carbon of imines, obtained by the DFT calculations, is 0.17, which is much lower than that of the carbon atom of carbonyls of 0.51. The activation of the α-C−H atom of HC═N unit of aldimines by organometallic reagents has never been reported. Herein, we describe the detailed study of our findings, including mechanistic investigations of the formations of **2** and **3** via DFT calculations, as well as the hydroboration reactions of aldehydes and ketones by pinacolborane (HBpin) catalyzed by **2**.

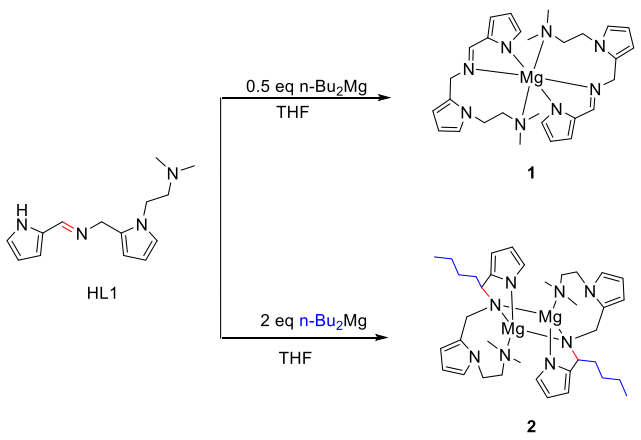
Scheme 1. Atomic Charges of the Central Carbon Atoms of Imines and Carbonyls Obtained by the DFT Calculations[7a]

RESULTS AND DISCUSSION

Synthesis and Structure of HL1. Initially, we conducted experiments for the synthesis of the ligand. The ligand 2-(2-((((1*H*-pyrrol-2-yl)methylene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine (HL1, Scheme S1) was generated by the condensation reaction between 2-(2-(amino-methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine[14] and 1*H*-pyrrole-2-carbaldehyde. The structure of the HL1 ligand was characterized by X-ray single-crystal diffraction (Figure S1) and NMR spectroscopy (Figures S6 and S7).

Syntheses and Structures of $[Mg(L1)_2]$ (1) and $[Mg_2(L2)_2]$ (2). Treatment of HL1 with 0.5 equiv of $^nBu_2Mg$ produced a mononuclear magnesium complex $[Mg(L1)_2]$ (**1**) (Scheme 2), which was isolated as a colorless solid after being recrystallized in toluene. When the ratio of HL1 to $^nBu_2Mg$ was increased to 1:2, a dinuclear compound $[Mg_2(L2)_2]$ (**2**) was afforded (Scheme 2).

Scheme 2. Syntheses of $[Mg(L1)_2]$ (1) and $[Mg_2(L2)_2]$ (2)



Single-crystal diffraction analysis revealed that complex **1** crystallizes in monoclinic crystal system of the *P*21/*n* space group. The structure of **1** is composed of one Mg(II) ion and two $[L1]^-$ ligands. The central Mg(II) ion is hexa-coordinated by six nitrogen atoms from two tridentate $[L1]^-$ ligands and displays an octahedron geometry (Figure 1a). Three pairs of coordinated nitrogen atoms originated from pyrrole, imine, and *N*,*N*-dimethylamine are *trans*-arranged. Thus, compound **1** shows approximate C_i symmetry.

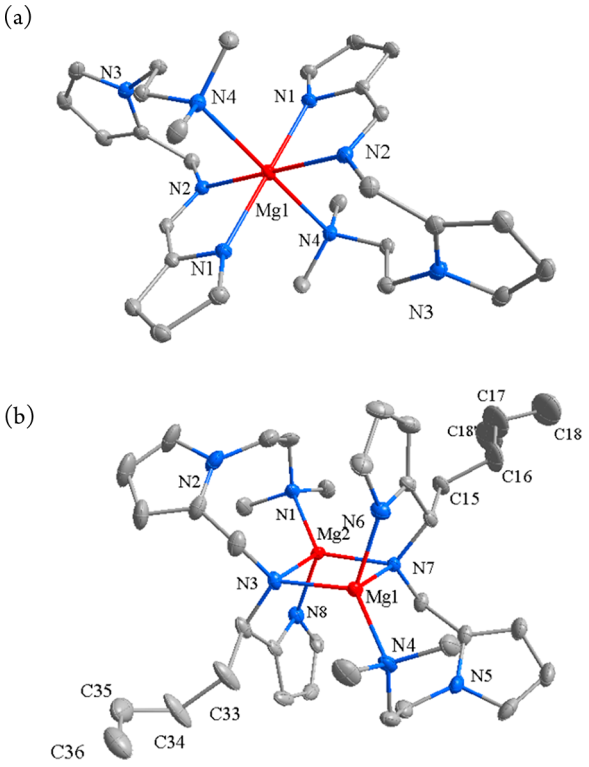


Figure 1. Solid-state structures of **1** (a) and **2** (b) with ORTEP diagram of 30% probability ellipsoid. Hydrogen atoms are omitted for clarity.

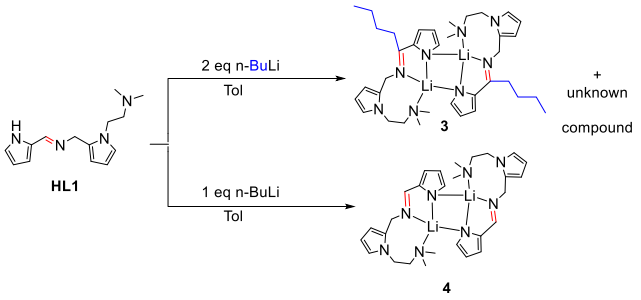
The crystal structure of **2** was determined by X-ray single-crystal diffraction analysis. An ORTEP representation of the structure of **2** is shown in Figure 1b. Complex **2** exhibits approximately C_i symmetry and consists of two Mg(II) ions and two newly formed $[L2]^{2-}$ ligands. Undoubtedly, the $[L2]^{2-}$ ligand was afforded by the nucleophilic addition of $^nBu_2Mg$ to the imine scaffold of the HL1 ligand. The geometry around each magnesium atom can be described as a distorted tetrahedron. Two magnesium atoms are doubly bridged by two amine nitrogen atoms of $[L2]^{2-}$ ligands, forming a rhombus-like configuration. The nucleophilic addition of $^nBu_2Mg$ to the C═N bond of the HL1 ligand was also confirmed by NMR spectroscopy (Figure S10).

Syntheses and Structures of $[Li_2(L3)_2]$ (3) and $[Li_2(L1)_2]$ (4). Intrigued by the expected observation of the nucleophilic addition of $^nBu_2Mg$ to the imine skeleton, we next endeavored to achieve this addition mediated by ^{n}BuLi. The 1:2 reaction between the HL1 ligand and ^{n}BuLi in toluene gave a new lithium compound $[Li_2(L3)_2]$ (**3**) (HL3 = 2-(2-(((1-

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

(1*H*-pyrrol-2-yl)pentylidene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethyl ethan-1-amine) and an unknown compound. Another new complex $[Li_2(L1)_2]$ (**4**) was afforded by the 1:1 reaction between the HL1 ligand and ^{n}BuLi (Scheme 3).

Scheme 3. Syntheses of $[Li_2(L3)_2]$ (3) and $[Li_2(L1)_2]$ (4)



Single-crystal X-ray diffraction analysis revealed that complex **3** crystallizes in the triclinic space group $P\bar{1}$ with Z = 1. Complex **3** is composed of two newly formed $[L3]^-$ ligands and two Li(I) ions (Figure 2a). The two symmetry-related Li(I) ions are doubly bridged by nitrogen atoms of pyrroles of two $[L3]^-$ ligands. The structure of **4** (Figure 2b) is similar to that of **3**, except that the hydrogen atom of the imine moiety of the HL1 ligand in **4** was not replaced by butyl group.

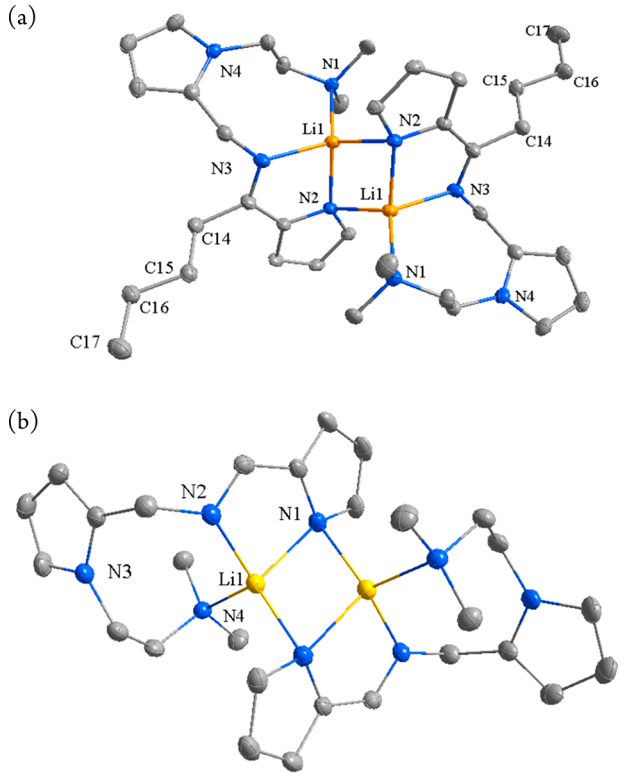
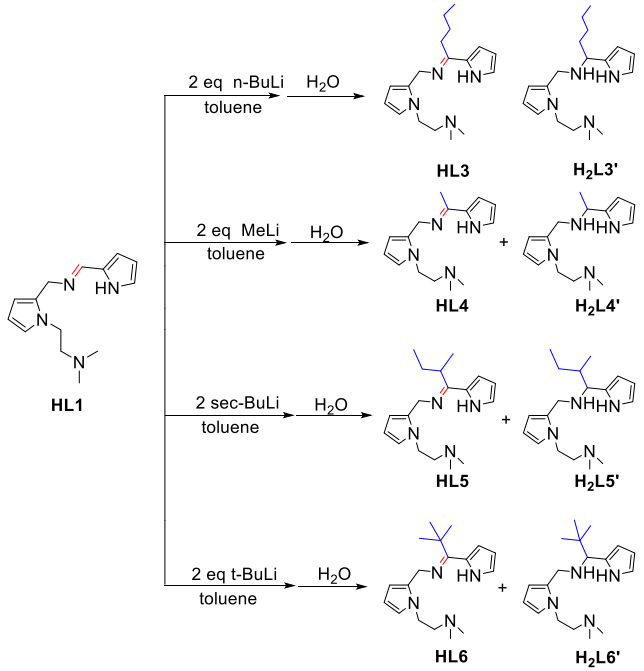


Figure 2. Solid-state structure of **3** (a) and **4** (b) with ORTEP diagram of 30% probability ellipsoid. Hydrogen atoms are omitted for clarity.

A remarkable structural feature of **3** is the presence of a (^{n}Bu)C═NR skeleton derived from the replacement of the hydrogen atom of the HC═N moiety by an *n*-butyl group. As mentioned above, due to the increased electrophilicity of the azomethine carbon of imines in comparison with that of aldehydes,[7a] it is not easy to abstract the hydrogen atom from the HC═N unit. The preparation of compound **3** demonstrates a new strategy for C−C coupling involving C−H bond activation of HC═N moiety.

Instructed by the work of Capriati and co-workers that the addition of ^{n}BuLi to imines could give amines,[13b] we suspected that the unknown compound found in the process for preparing **3** is an amine compound. Thus, we reconducted the reaction between HL1 and 2 equiv of ^{n}BuLi and hydrolyzed the reaction mixture directly. An amine compound *N*-((1-(2-(dimethylamino)ethyl)-1*H*-pyrrol-2-yl)methyl)-1-(1*H*-pyrrol-2-yl)pentan-1-amine (H_2L3', Scheme 4) was isolated, which was characterized by NMR spectroscopy and HRMS.

Scheme 4. Syntheses of HL3−H_2L6′



To expand the scope of the nucleophilic addition and α-C−H substitution reactions of the HL1 ligand, we conducted the 1:2 reactions of the HL1 ligand with MeLi, *sec*-BuLi, and *tert*-BuLi, respectively, and hydrolyzed the reaction mixtures directly. A series of imines HL4−HL6 and amines H_2L4'−H_2L6' (Scheme 4) were afforded. They were characterized by NMR spectroscopy and HRMS. It was found that the amines were the major products.

Mechanistic Insights from DFT Calculations. DFT calculations were carried out to better understand the divergent results in reactions of ^{n}BuLi and ^{n}Bu$_2$Mg with HL1, and methyllithium and dimethylmagnesium were used as model organometallic reagents. When the lithium reagent is involved (Figure 3), the formation of **(L1)Li** by deprotonation of HL1 with methyllithium should be formed first. Incorporation of another methyllithium with **(L1)Li** forms a more stable complex **9-Li**, in which the two lithium atoms are bridged by the methyl group. The addition of $LiCH_3$ to the imino functionality occurs via **TS1-Li**, which is 26.1 kcal/mol above that of **9-Li** and exergonically forms complex **10-Li**. From the latter intermediate, the regeneration of the imino functionality could possibly occur by elimination of LiH via

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

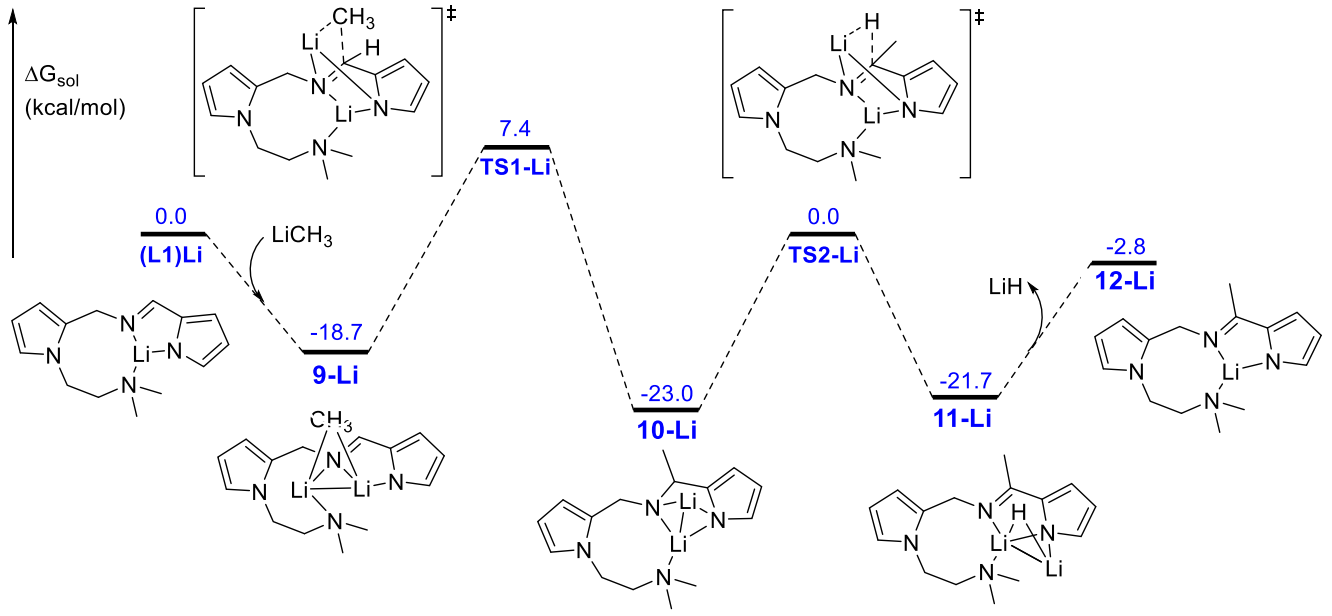


Figure 3. DFT results for the reaction of $LiCH_3$ with HL1. Solvation free energies (in kcal/mol) are relative to free $LiCH_3$ with HL1.

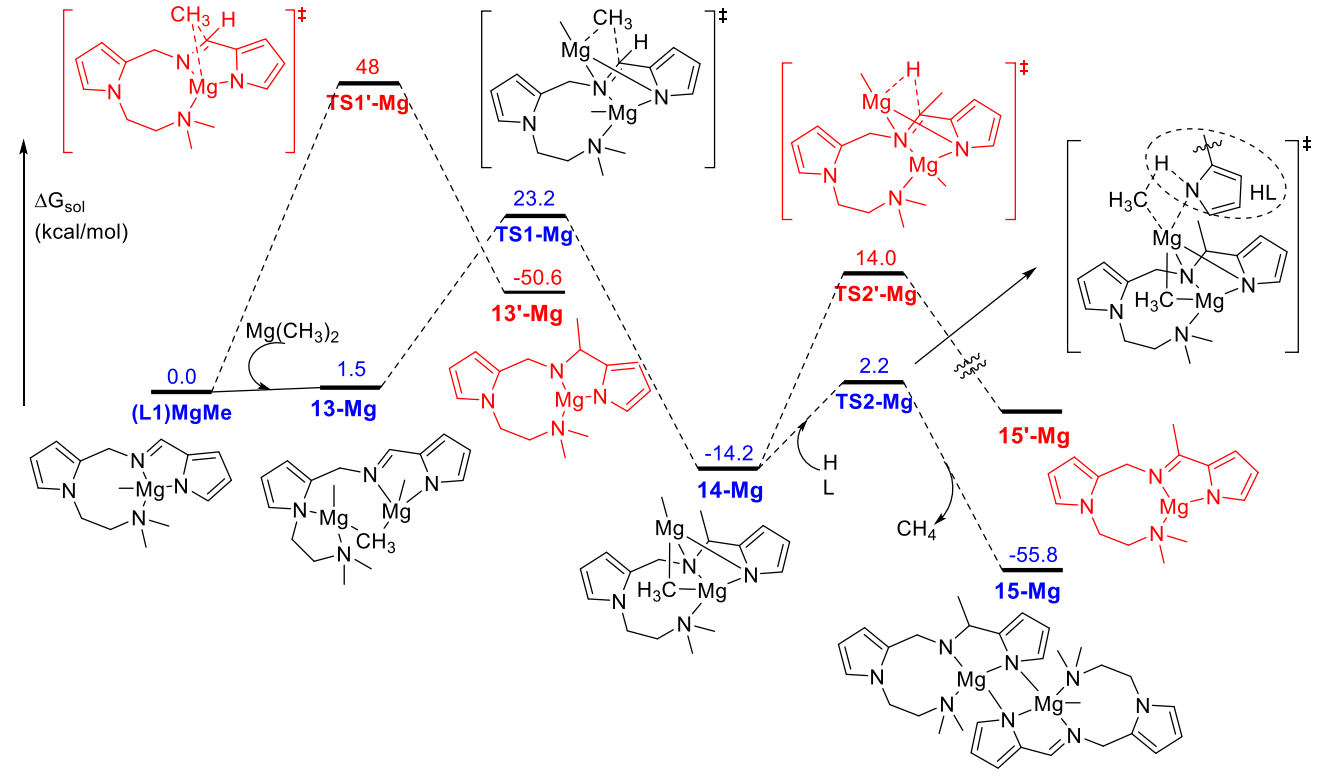


Figure 4. DFT results for the reaction of $Mg(CH_3)_2$ with HL1. Solvation free energies (in kcal/mol) are relative to free $Mg(CH_3)_2$ with HL1.

TS2-Li, which requires an activation barrier of 23.0 kcal/mol and leads to intermediate **11-Li**. After releasing of LiH from **11-Li**, **12-Li** could be formed before its final dimerization to complex **3**.

In reaction of dimethylmagnesium with HL1 (Figure 4), upon the formation of complex **(L1)MgMe**, the direct addition of the $Mg(CH_3)_2$ moiety to the imino functionality via **TS1′-Mg** is very difficult as a high barrier of 48.0 kcal/mol was predicted, which could be attributed to the fact that the Mg chelates tightly with three nitrogen atoms in **(L1)MgMe** making difficult the approach of the $Mg(CH_3)_2$ moiety to the π orbital of the C═N unit. Instead, the incorporation of another $Mg(CH_3)_2$ forms first a bridged complex, **13-Mg**, from which the addition of Mg and methyl to the C═N functionality could be realized via **TS1-Mg** with a barrier of 21.7 kcal/mol. After the formation of intermediate **14-Mg**, it was found that the regeneration of the C═N functionality by a similar β-H elimination as described in reaction of lithium reagent is more difficult, as the **TS2′-Mg** is 28.2 kcal/mol higher than **14-Mg**. However, the deprotonation of another HL1 ligand by one of the remaining methyl groups in the complex is much more facile via **TS2-Mg** with a lower barrier of 16.4 kcal/mol and

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

exergonically forms intermediate **15-Mg** highly, from which complex **2** could be finally expected by further transformations. The energy profile explains well that no C═N contained in reaction with magnesium reagent is attributed to the difficult β-H elimination of **14-Mg** as in competition with the facile NH deprotonation of pyrrole in HL1.

Hydroboration of Aldehydes and Ketones. Motivated by the successful preparation of **1**−**4** with **2** and **3** displaying intriguing structural features, we endeavored to employ **2** as catalyst for the hydroboration of carbonyl compounds.[15,16] Several lithium and magnesium complexes were reported to affect the hydroboration of carbonyl compounds.[17−24] Encouraged by these examples, we screened **2** for catalytic activity. 4-Chlorobenzaldehyde (0.25 mmol), pinacolborane (0.25 mmol), and 0.0025 mol of **2** in $CDCl_3$ (0.5 mL) were loaded in a J. Young's NMR tube, and the ^{1}H NMR spectrum was determined at room temperature. It was found that the hydroboration underwent promptly, affording corresponding borate ester in 99% yield within 30 min (Table 1, entry 1).

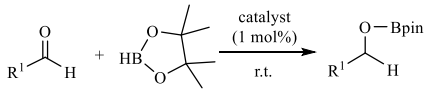
To explore the generality of the hydroboration protocol, a range of aldehydes were subjected to hydroboration with pinacolborane using **2** as catalyst. The results are summarized in Table 1. In virtually all cases, hydroboration of aldehydes proceeded smoothly, generating corresponding borate ester in almost quantitative yield. Benzaldehydes bearing electron-withdrawing (**5a** and **5b**) and electron-releasing groups (**5d** and **5e**) were well-tolerated. Pyridine-2-aldehyde (**5f**) was selectively hydroborated on the aldehyde, leaving the imine group unattacked. Furthermore, the aldehyde group of pyrrole-2-aldehyde (**5g**) was chemoselectively hydroborated, leaving the NH moiety unaffected. Similarly, when two aldehyde groups are attached to pyrrole or benzene ring (**5h** and **5i**), we obtained the dihydroborated products exclusively (>99% yield) by adding 2 equiv of pinacolborane.

In light of the successful results of aldehydes, we next examined the potentials of **2** for the hydroboration of ketones (Table 2). The studies of other groups revealed that the hydroboration of ketones was slower than that of aldehydes. To our delight, results of several different ketones demonstrate a broad scope of this protocol. In all cases, the desired borate ester products were exclusively obtained (97−99%) within 30 min at room temperature under the catalyst loading of 1 mol %. Alkyl ketones are compatible with this system; acetone (**7a**) and cyclohexanone (**7f**) were cleanly converted to the corresponding borate ester in >99% yields within 30 min. Acetophenone bearing electron-donating (**7e**) and electron-withdrawing groups (**7c** and **7d**) proceeded well. Diary ketones (**7h**−**7k**) were completely converted to the corresponding borate esters. Remarkably, the steric hindered ketones also underwent hydroboration smoothly within 30 min in good to excellent yield (**7k**). In addition, extraordinary chemoselectivity was observed for 1-(pyridin-2-yl)ethan-1-one (**7g**); the carbonyl group was hydroborated, leaving the imine moiety nonreduced.

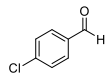
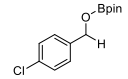
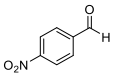
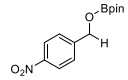
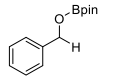
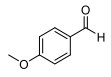
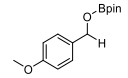
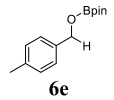
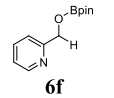
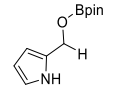
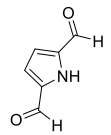
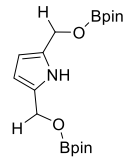
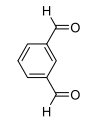
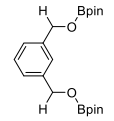
Inspired by the successful results for the hydroboration of aldehydes and ketones, we sought to further explore the catalyst selectivity between aldehydes and ketones. To this end, the stoichiometric amount of benzaldehyde and acetophenone were subjected to hydroboration by using **2** (1 mol %) as catalyst. It is found that 97% hydroboration of aldehydes occurred for 2. Similar results were observed when 4-chlorobenzaldehyde and 4-chloroacetophone were reacted with HBPin in a 1:1:1 molar ratio. Meanwhile, the 1:1:1 reaction of pyridine-2-aldehyde, 1-(pyridin-2-yl)ethan-1-one and HBpin were examined, and exclusive hydroboration of pyridine-2-aldehyde was achieved. Analogous results were found for the reaction of 4-methylbenzaldehyde, 4-methyl-acetonphone and HBpin (1:1:1). The intramolecular selectivity of the aldehyde over ketone was also realized for the 1:1 4-acetyl benzaldehyde and HBpin, and the aldehyde group was hydroborated in 99% yield. Naturally, the ketone functionality of 4-acetyl benzaldehyde was also reduced, when the molar ratio of 4-acetyl benzaldehyde and HBPin was changed to 1:2 (Scheme 5).

The catalytic activity of **1** toward the hydroboration reaction of carbonyl compounds were also examined. It is found that

Table 1. Hydroboration of Aldehydes Catalyzed by Complex 2[a]



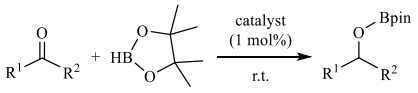
5 6

Entry	Reactant	Cat (1 mol%)	Product[b]	Yield[b] (%)
1	 **5a**	**2**	 **6a**	>99
2	 **5b**	**2**	 **6b**	>99
3	 **5c**	**2**	 **6c**	>99
4	 **5d**	**2**	 **6d**	>99
5	 **5e**	**2**	 **6e**	>99
6	 **5f**	**2**	 **6f**	>99
7	 **5g**	**2**	 **6g**	>99
8	 **5h**	**2**	 **6h**	>99
9	 **5i**	**2**	 **6i**	>99

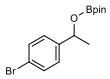
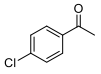
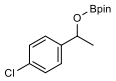
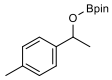
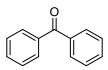
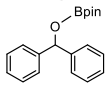
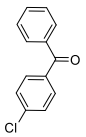
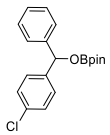
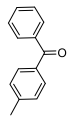
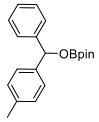
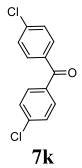
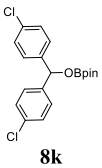
[a]Conditions: aldehydes (0.25 mmol), HBpin (0.25 mmol), and catalyst (0.0025 mmol) in $CDCl_3$(0.5 mL), 30 min. [b]Yields of the borate esters based on ^{1}H NMR analysis.

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

Table 2. Hydroboration of Ketones Catalyzed by Complex 2[a]



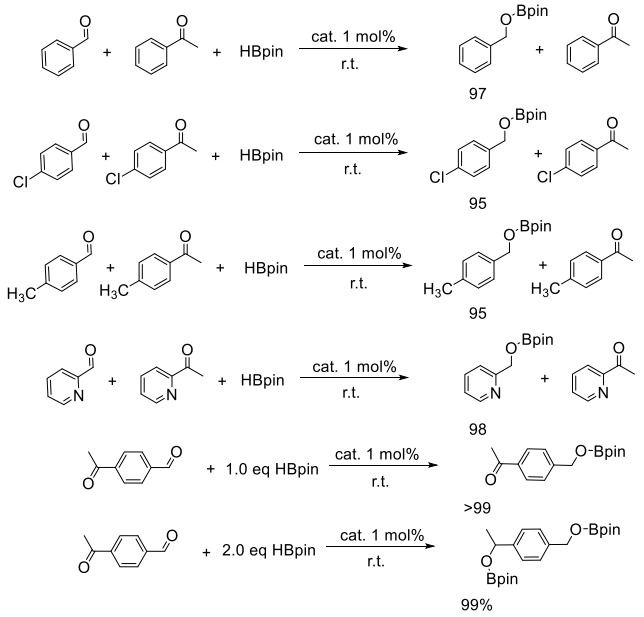
7 8

Entry	Reactant	Cat (1 mol%)	Product[b]	Yield[b] (%)
1	 7a	2	 8a	>99
2	 7b	2	 8b	>99
3	 7c	2	 8c	>99
4	 7d	2	 8d	>99
5	 7e	2	 8e	>99
6	 7f	2	 8f	>99
7	 7g	2	 8g	>99
8	 7h	2	 8h	>99
9	 7i	2	 8i	>99
10	 7j	2	 8j	97
11	 7k	2	 8k	99

[a]Conditions: ketones (0.25 mmol), HBpin (0.25 mmol) and catalysts (0.0025 mmol) in $CDCl_3$ (0.5 mL), 30 min. [b]Yields of the products based on ^1H NMR analysis.

compound **1** shows very high catalytic activity for the hydroboration of benzaldehyde (**5c**, Figure S46) and cyclohexanone (**7f**, Figure S47).

Scheme 5. Chemoselective Hydroboration of Aldehydes and Ketones Catalyzed by Complex 2[a]



[a]Conditions: aldehyde (0.25 mmol), ketones (0.25 mmol), HBpin (0.25 mmol) and catalyst (0.0025 mmol) in $CDCl_3$ (0.5 mL). [b]Yields of the products based on ^1H NMR analysis.

CONCLUSIONS

In conclusion, the α-C−H substitution of the HC═NR skeleton of the Schiff base ligand HL1 mediated by a series of organolithium reagents were realized, giving C−C coupling products that involving inert C−H bond activation of the HC═NR moiety. In addition, the successful conversion of imine into amine was achieved through nucleophilic addition of ^{n}Bu$_2$Mg and organolithium reagents to the C═N bond of the HL1 ligand. The mechanisms for the formations of **2** and **3** were rationalized by DFT calculations. Complex **2** demonstrated its competence as a catalyst toward the hydroboration of aldehydes and ketones. The key advantages of this protocol are mild reaction conditions, extremely high yields, wide functional group tolerance, and high selectivity for aldehyde over ketone. The very good economy, great earth abundance, and nontoxic natures of lithium and magnesium render them as ideal alternatives to replace precious metal catalysts in some organic reactions.

EXPERIMENTAL SECTION

General Methods. All the reactions were performed in a N_2-filled Vigor glovebox. THF, hexane, and toluene were dried over purple sodium benzophenone ketyl and stored with 4 Å molecular sieves. ^{n}Bu$_2$Mg, ^{n}BuLi, MeLi, *sec*-BuLi, and *tert*-BuLi were purchased from J&K and Macklin chemical and directly used as received. Deuterochloroform was dried over CaH_2 before distilled under vacuum and stored with 4 Å molecular sieves. ^1H NMR spectra were recorded at the ambient temperature on Bruker Avance-III 400 MHz and Aglient 400 and 300 MHz instruments and the spectra were referenced to the TMS signal (0 ppm). ^{13}C NMR spectra were recorded at the ambient temperature on Bruker Avance-III 600 MHz NMR spectrometer. Elemental analyses for C, H, and N were carried out on a PerkinElmer 2400 analyzer. Crystal determination was performed with a Bruker SMART APEX II CCDC diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). HRMS spectrum was obtained by TOF-MS. The detailed

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837

procedure for the synthesis of the HL1 ligand was provided in the Supporting Information.

Synthesis of [Mg(L1)$_2$] (1). At −35 °C, HL1 (0.2444 g, 1.0 mmol) was dissolved in THF (2 mL). Then ^{n}Bu$_2$Mg (0.5 mL, l.0 M in hexane, 0.5 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum, and the resulting crude product was washed with *n*-hexane to give a white powder. Yield: 0.21 g (83%). Colorless crystals were obtained in toluene at room temperature. The structure of **1** was determined by X-ray single-crystal diffraction. Anal. Calcd for $C_{28}H_{38}MgN_8$: C, 65.82; H, 7.50; N, 21.93. Found: C, 65.50; H, 7.58; N, 21.38.

Synthesis of [Mg$_2$(L2)$_2$] (2). At −35 °C, HL1 (0.2444 g, 1.0 mmol) was dissolved in THF (2 mL). Then ^{n}Bu$_2$Mg (2 mL, l.0 M in hexane, 2 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum, and the resulting crude product was washed with *n*-hexane to give a white powder. Yield: 0.28 g (85%). Colorless crystals were obtained in toluene at room temperature. The structure of **2** was determined by X-ray single-crystal diffraction. Anal. Calcd for $C_{36}H_{56}Mg_2N_8$: C, 66.57; H, 8.69; N, 17.25. Found: C, 66.18; H, 8.53; N, 16.92.

Synthesis of [Li$_2$(L3)$_2$] (3) and Characterization of HL3. At −35 °C, HL1 (0.2444 g, 1.0 mmol) was dissolved in toluene (2 mL). Then ^{n}BuLi (1.0 mL, 2.4 M in hexane, 2.4 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum, and the resulting crude product was washed with *n*-hexane to give 0.224 g of a red powder. Colorless crystals were obtained in toluene at room temperature. The structure of **3** was obtained by X-ray single-crystal diffraction. ^{1}H and ^{13}C NMR spectra of **3** are very complicated. Thus, the compound was characterized by being hydrolyzed to HL3. Complex **3** was hydrolyzed with water (3 mL) and extracted with DCM (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum to give a yellow oil. HRMS (EI) Calcd for: $C_{18}H_{28}N_4$ [HL3] 300.2314. Found: 300.2312.

Synthesis of [Li$_2$(L1)$_2$] (4). At −35 °C, HL1 (0.1222 g, 0.5 mmol) was dissolved in toluene (2 mL). Then ^{n}BuLi (0.32 mL, l.6 M in hexane, 0.5 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight, produced a pink powder. Volatiles were removed under vacuum, and the resulting crude product was washed with toluene/hexane to give a light pink powder. Yield: 0.083 g (66%). Colorless crystals were obtained in toluene at room temperature. The structure of **4** was determined by X-ray single-crystal diffraction. Anal. Calcd for $C_{28}H_{38}Li_2N_8$: C, 67.19; H, 7.65; N, 22.39. Found: C, 66.76; H, 7.73; N, 22.32.

General Procedure for the Hydroboration Reaction. In a nitrogen-filled dry box, pinacol borane (HBpin, 0.032 g, 0.25 mmol), aldehyde or ketone substrate (0.25 mmol), catalyst (0.0025 mmol), and $CDCl_3$ (0.5 mL) were added to a J. Young NMR tube. The tube was taken out from the glovebox and was shaken for 30 min. Then the ^{1}H NMR spectrum of the mixture was recorded. The yield of the product was calculated by comparing the area of the Bpin of the product with that of the unreacted HBpin.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00815.

Crystal data and data collection details for the HL1 ligand, newly formed HL3−H$_2$L6′ ligands and compounds **1**−**4**. ^{1}H NMR and ^{13}C NMR spectra of the compounds and products (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 2052855−2052858 and 2080621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Yahong Li − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*; orcid.org/0000-0002-6467-0607; Email: liyahong@suda.edu.cn

Yuanzhi Xia − *College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, PR China*; orcid.org/0000-0003-2459-3296; Email: xyz@wzu.edu.cn

Authors

Yan Dang − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Yalan Wang − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Yafei Li − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Man Xu − *College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, PR China*

Chaohong Jia − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Yanhua Lu − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Liang Zhang − *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00815

Author Contributions

[§]Y.D. and Y.W. contributed equally to this paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors appreciate the financial support from Natural Science Foundation of China (21772140 and 21873074), Natural Science Foundation of Jiangsu Province of China (BK20171213), a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institution, and the project of scientific and technologic infrastructure of Suzhou (SZS201905).

■ REFERENCES

(1) Ejidike, I. P.; Ajibade, P. A. Transition Metal Complexes of Symmetrical and Asymmetrical Schiff Bases as Antibacterial, Antifungal, Antioxidant, and Anticancer Agents: Progress and Prospects. *Rev. Inorg. Chem.* **2015**, *35*, 191−224.

(2) Martin, S. F. Recent Applications of Imines as Key Intermediates in the Synthesis of Alkaloids and Novel Nitrogen Heterocycles. *Pure Appl. Chem.* **2009**, *81*, 195−204.
(3) (a) Enders, D.; Reinhold, U. Asymmetric Synthesis of Amines by Nucleophilic 1,2-addition of Organometallic Reagents to the CN-Double Bond. *Tetrahedron: Asymmetry* **1997**, *8*, 1895−1946. (b) Bloch, R. Additions of Organometallic Reagents to C═N Bonds: Reactivity and Selectivity. *Chem. Rev.* **1998**, *98*, 1407−1438. (c) Rappoport, E. Z. *The Chemistry of Anilines, Parts 1 and 2*; John Wiley & Sons: New York, 2007. (d) Ferraris, D. Catalytic, Asymmetric Alkylation of Imines. *Tetrahedron* **2007**, *63*, 9581−9597.
(4) (a) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. Catalytic Enantioselective Formation of C-C Bonds by Addition to Imines and Hydrazones: A Ten-Year Update. *Chem. Rev.* **2011**, *111*, 2626−2704. (b) Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M. Catalytic Enantioselective Allylation of Ketoimines. *J. Am. Chem. Soc.* **2006**, *128*, 7687−7691. (c) Reid, J. P.; Simón, L.; Goodman, J. M. A Practical Guide for Predicting the Stereochemistry of Bifunctional Phosphoric Acid Catalyzed Reactions of Imines. *Acc. Chem. Res.* **2016**, *49*, 1029−1041.
(5) Patel, N. R.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. Mild, Redox-Neutral Alkylation of Imines Enabled by an Organic Photocatalyst. *ACS Catal.* **2017**, *7*, 1766−1770.
(6) (a) Han, B. W.; Li, Y. J.; Yu, Y.; Gong, L. Photocatalytic Enantioselective α-Aminoalkylation of Acyclic Imine Derivatives by A Chiral Copper Catalyst. *Nat. Commun.* **2019**, *10*, 3804. (b) Friestad, G. K. Addition of Carbon-Centered Radicals to Imines and Related Compounds. *Tetrahedron* **2001**, *57*, 5461−5496. (c) Miyabe, H.; Ueda, M.; Naito, T. Carbon-Carbon Bond Construction Based on Radical Addition to C═N Bond. *Synlett* **2004**, *7*, 1140−1157.
(7) (a) Yamada, K.; Tomioka, K. Copper-Catalyzed Asymmetric Alkylation of Imines with Dialkylzinc and Related Reactions. *Chem. Rev.* **2008**, *108*, 2874−2886. (b) Côté, A.; Charette, A. B. General Method for the Expedient Synthesis of Salt-Free Diorganozinc Reagents Using Zinc Methoxide. *J. Am. Chem. Soc.* **2008**, *130*, 2771−2773.
(8) Takahashi, T.; Liu, Y. H.; Xi, C. J.; Huo, S. Q. Grignard Reagent Mediated Reaction of $Cp_2Zr(II)$-Ethylene Complex with Imines. *Chem. Commun.* **2001**, 31−32.
(9) (a) Rutherford, J. L.; Hoffmann, D.; Collum, D. B. Consequences of Correlated Solvation on the Structures and Reactivities of RLi-Diamine Complexes: 1,2-Addition and α-Lithiation Reactions of Imines by TMEDA-Solvated n-Butyllithium and Phenyllithium. *J. Am. Chem. Soc.* **2002**, *124*, 264−271. (b) Cogan, D. A.; Ellman, J. A. Asymmetric Synthesis of α,α-Dibranched Amines by the Trimethylaluminum-Mediated 1,2-Addition of Organolithiums to tert-Butanesulfinyl Ketimines. *J. Am. Chem. Soc.* **1999**, *121*, 268−269. (c) Denmark, S. E.; Nakajima, N.; Nicaise, O. J. C. Asymmetric Addition of Organolithium Reagents to Imines. *J. Am. Chem. Soc.* **1994**, *116*, 8797−8798. (d) Orr, S. A.; Border, E. C.; Andrews, P. C.; Blair, V. L. Lithium-Bromide Exchange versus Nucleophilic Addition of Schiff's Base: Unprecedented Tandem Cyclisation Pathways. *Chem. - Eur. J.* **2019**, *25*, 11876−11882.
(10) (a) Wu, G.; Huang, M. S. Organolithium Reagents in Pharmaceutical Asymmetric Processes. *Chem. Rev.* **2006**, *106*, 2596−2616. (b) Dickstein, J. S.; Kozlowski, M. C. Organometal Additions to α-iminoesters: N-alkylation via Umpolung. *Chem. Soc. Rev.* **2008**, *37*, 1166−1173. (c) Kobayashi, S.; Ishitani, H. Catalytic Enantioselective Addition to Imines. *Chem. Rev.* **1999**, *99*, 1069−1094.
(11) Vidal, C.; García-Alvarez, J.; Hernán-Gómez, A.; Kennedy, A. R.; Hevia, E. Exploiting Deep Eutectic Solvents and Organolithium Reagent Partnerships: Chemoselective Ultrafast Addition to Imines and Quinolines Under Aerobic Ambient Temperature Conditions. *Angew. Chem., Int. Ed.* **2016**, *55*, 16145−16148.
(12) Dilauro, G.; Dell'Aera, M.; Vitale, P.; Capriati, V.; Perna, F. M. Unprecedented Nucleophilic Additions of Highly Polar Organometallic Compounds to Imines and Nitriles Using Water as a Non-Innocent Reaction Medium. *Angew. Chem., Int. Ed.* **2017**, *56*, 10200−10203.
(13) (a) Desmarchelier, A.; Ortiz, P.; Harutyunyan, S. R. Tertiary α-Diarylmethylamines Derived from Diarylketimines and Organomagnesium Reagents. *Chem. Commun.* **2015**, *51*, 703−706. (b) Cicco, L.; Salomone, A.; Vitale, P.; Ríos-Lombardía, N.; González-Sabín, J.; García-Alvarez, J.; Perna, F. M.; Capriati, V. Addition of Highly Polarized Organometallic Compounds to *N*-tert-Butanesulfinyl Imines in Deep Eutectic Solvents under Air: Preparation of Chiral Amines of Pharmaceutical Interest. *ChemSusChem* **2020**, *13*, 3583−3588.
(14) 2-(2-(Aminomethyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine was synthesized from (1*H*-pyrrol-2-yl)methanamine and 2-chloro-*N*,*N*-dimethylethan-1-amine. See the Supporting Information for details.
(15) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238−3259.
(16) Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15−34.
(17) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Koehn, G. Magnesium-Catalyzed Hydroboration of Aldehydes and Ketones. *Chem. Commun.* **2012**, *48*, 4567−4569.
(18) Osseili, H.; Mukherjee, D.; Spaniol, T. P.; Okuda, J. Ligand Influence on Carbonyl Hydroboration Catalysis by Alkali Metal Hydridotriphenylborates $[(L)M][HBPh_3]$ (M = Li, Na, K). *Chem. - Eur. J.* **2017**, *23*, 14292−14298.
(19) Harinath, A.; Bhattacharjee, J.; Nayek, H. P.; Panda, T. K. Alkali Metal Complexes as Efficient Catalysts for Hydroboration and Cyanosilylation of Carbonyl Compounds. *Dalton Trans.* **2018**, *47*, 12613−12622.
(20) Bisai, M. K.; Das, T.; Vanka, K.; Sen, S. S. Easily Accessible Lithium Compound Catalyzed Mild and Facile Hydroboration and Cyanosilylation of Aldehydes and Ketones. *Chem. Commun.* **2018**, *54*, 6843−6846.
(21) Zhu, Z. Y.; Wu, X. L.; Xu, X. J.; Wu, Z. J.; Xue, M. Q.; Yao, Y. M.; Shen, Q.; Bao, X. G. n-Butyllithium Catalyzed Selective Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83*, 10677−10683.
(22) Luo, M.; Li, J.; Xiao, Q.; Yang, S. L.; Su, F.; Ma, M. T. Efficient and Selective Carbonyl Hydroboration Catalyzed by a Lithium NCN-Pincer Magnesium Complex $[Li(THF)_4][NCN\text{-}MgBr_2]$. *J. Organomet. Chem.* **2018**, *868*, 31−35.
(23) Li, J.; Luo, M.; Sheng, X. C.; Hua, H. M.; Yao, W. W.; Pullarkat, S. A.; Xu, L.; Ma, M. T. Unsymmetrical β-Diketiminate Magnesium-(I) Complexes: Syntheses and Application in Catalytic Hydroboration of Alkyne, Nitrile and Carbonyl Compounds. *Org. Chem. Front.* **2018**, *5*, 3538−3547.
(24) Yadav, S.; Dixit, R.; Bisai, M. K.; Vanka, K.; Sen, S. S. Alkaline Earth Metal Compounds of Methylpyridinato β-Diketiminate Ligands and Their Catalytic Application in Hydroboration of Aldehydes and Ketones. *Organometallics* **2018**, *37*, 4576−4584.

https://doi.org/10.1021/acs.organomet.0c00815
Organometallics 2021, 40, 1830−1837