Inorganic Chemistry
Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX
Article
pubs.acs.org/IC

# Well-Defined Amidate-Functionalized N-Heterocyclic Carbene -Supported Rare-Earth Metal Complexes as Catalysts for Efficient Hydroboration of Unactivated Imines and Nitriles

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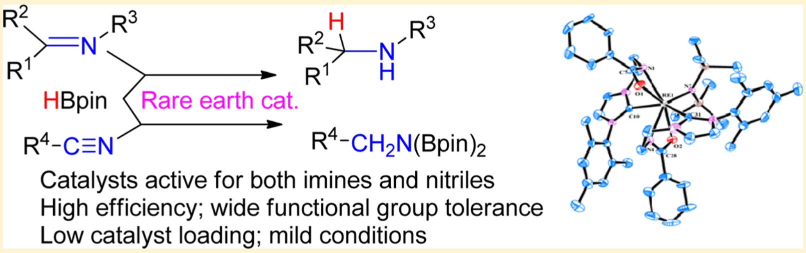
*Supporting Information*



**ABSTRACT:** Four amidate-functionalized N-heterocyclic carbene (NHC) rare-earth metal amido complexes $[(\kappa^2\text{-N,O-}\kappa^1\text{-}\mathbf{L})_2\text{REN(SiMe}_3)_2]$ ($\mathbf{L}$ = 1-$(C_6H_5C{=}ONCH_2CH_2)$-3-$(CH_3)_3C_6H_2(N(CH)_2NC))$ [RE = Er (**1**), Y (**2**), Dy (**3**), Gd (**4**)] were synthesized by one-pot reactions of 2 equiv of (1-$(C_6H_5C{=}ONHCH_2CH_2)$-3-$(CH_3)_3C_6H_2$-$(N(CH)_2NCH))$Br ($H_2$**L**Br) with 5 equiv of $KN(SiMe_3)_3$ followed by treatment with 1 equiv of $RECl_3$ in tetrahydrofuran at −40 °C. These complexes were fully characterized, and their catalytic activities toward hydroboration of unactivated imines and nitriles were investigated, and it was found that these complexes displayed excellent activities as well as remarkable functional group compatibility for imine and nitrile substrates such as halo-, alkyl-, hydroxyl-, *N,N*-dimethylamino-, and nitro- substituents. Among those, the chemoselectivity for this reaction among the common unsaturated functional groups was achieved in the order $C{=}O \gg C{=}N > C{\equiv}N > CO_2Et > C{=}C$ in the current catalytic system, which may facilitate their further application in synthetic chemistry.

## INTRODUCTION

Amines are very important building blocks present not only in many natural products such as proteins, nucleic acids, and alkaloids but also in key synthetic intermediates for chemicals such as bactericides, herbicides, rubber accelerators, and surface-active agents. Most of the clinically applicable drugs are also amines or amine derivatives. Many applied metal complexes or catalysts contain amines or their derivatives as supporting ligands.[1] Therefore, the mastery of the synthesis of amines is an essential step in both academic and industrial fields.[2]

Among the various methods developed for the preparation of amines, the reduction of nitrogenous compounds is a crucial one. The reduction can be performed using stoichiometric alkaline metal hydrides, such as $LiAlH_4$ or $NaBH_4$, as reducing reagents, yet these reagents generally display poor selectivity and sometimes result in low yields of the desired products.[3] Catalytic hydrogenation can selectively reduce unsaturated nitrogenous bonds in a controlled manner.[1b,4−7] The catalytic hydroboration of nitriles and imines is a common method for the synthesis of primary and secondary amines.[8−10] Though various catalytic systems based on magnesium,[11] ruthenium,[12] molybdenum,[13] cobalt complexes,[14] and the frustrated Lewis pairs[15] exhibited different activities toward imines or nitriles, nevertheless, these catalysts for the hydroboration of nitriles or imines usually require long reaction time (12−72 h) and high catalyst loading (up to 20 mol %), yet their selectivity toward diverse unsaturated bonds were still poor. More importantly, few catalysts were shown to be active in the hydroboration of both imines and nitriles. To this end, it is, therefore, of importance to develop some more general catalytic systems featuring both high activity and a broader substrate scope.

Rare-earth metal complexes have been widely used in organic synthesis,[16] such as in the hydrogenation of olefins,[17] hydrosilylation,[18] hydroamination,[19] and hydroboration.[20] Organo-rare-earth metal catalysts have been reported to catalyze the

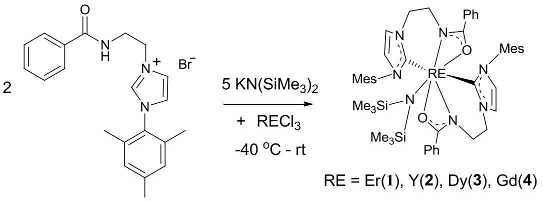
**Received:** July 22, 2018

hydroboration of ketones and aldehydes.[20] However, it was found very recently that the hydroboration of aldehydes could be efficiently performed without the catalyst and solvent, but ketone substrates are less reactive under the same conditions.[21] In contrast to ketones or aldehydes, imines bear substituents on either side of the C═N bond, showing distinct steric and electronic properties. Because of the steric hindrance of the imine, their interactions with the catalysts are normally less favored than those in the case of ketones or aldehydes. This steric hindrance issue is even more pronounced for nitriles, when considering the initial formed reaction intermediate, RCH═NBpin (Bpin = pinacolboranyl) in the hydroboration reaction.[10,11c,12c,13a] For this reason, nitriles are more difficult to be reduced. We report the design and the synthesis of a series of amidate-functionalized N-heterocyclic carbene (NHC) rare-earth metal amido complexes that exhibit excellent catalytic activity in the hydroboration of both imines and nitriles. Halo-, hydroxyl-, amino-, and nitro- groups were all remarkably tolerated in these reactions when highly electropositive rare-earth metal complexes were applied. To the best of our knowledge, fewer examples of rare-earth metal catalysts have been developed for the hydroboration of imines or nitriles.[22]

## ■ RESULTS AND DISCUSSION

**Synthesis and Characterization of Rare-earth Metal Complexes.** Four amidate-functionalized NHC rare-earth metal amido complexes $[(\kappa^2\text{-N,O-}\kappa^1\text{-}\mathbf{L})_2\text{REN}(\text{SiMe}_3)_2]$ ($\mathbf{L}$ = 1-($C_6H_5C$═$ONCH_2CH_2$)-3-$(CH_3)_3C_6H_2(N(CH)_2NC)$) (RE = Er (**1**), Y (**2**), Dy (**3**), Gd (**4**)) were synthesized through one-pot reaction of the ligand precursor, $RECl_3$ and $KN(SiMe_3)_2$ (KHMDS) (Scheme 1). All complexes were readily crystallized from tetrahydrofuran (THF)/*n*-hexane to afford analytically pure products in moderate yield. The diamagnetic complex **2** was further characterized by NMR spectroscopy, where the $^{13}C$ NMR spectrum showed a $C_{carbene}$ resonance at 197.2 ppm, resonating as the doublet ($^1J_{YC}$ = 27.5 Hz). Previous work[23] showed doublet carbene carbon resonances with the coupling constant larger than the data found in this work. All complexes were also characterized by IR spectroscopy and elemental analyses. In all cases, the loss of the N−H stretch from the proligand and the weakening of the C═O stretch was evident (e.g., C═O stretch: 1645−1655 $cm^{-1}$ for **1**−**4**).

**Scheme 1. Synthesis of Complexes 1−4**



RE = Er(**1**), Y(**2**), Dy(**3**), Gd(**4**)

Solid-state structure of complexes **1**−**4**, confirmed by X-ray diffraction analyses (Figures 1 and S101−S104 in the Supporting Information), are essentially isomorphous. All rare-earth metal centers are seven-coordinate with two carbene carbon atoms, two $\kappa^2$-bonded amidate groups, and an additional amido group. The coordination of the ethereal solvent molecule THF was not observed in all complexes, even though the preparations were performed in THF, indicating relatively stronger interaction between the ligand and the rare-earth metals in **1**−**4**. This result is in sharp contrast to the Rh(I) complex bearing the same ligand as the amidate group in the latter binds in a $\kappa^1$-fashion via the N atom.[24] This result is similar to the yttrium complex in which amidate groups $\kappa^2$-bonded with yttrium.[25] The seven-coordinate $P6_5$ symmetric molecular structure of **1**−**4** confirms electron delocalization through the $\kappa^2$-amidate backbone as indicated by the C−O and C−N bond lengths (C−O bond lengths of amidate from 1.260(15) to 1.319(12) Å and C−N bond lengths of amidate from 1.265(14) to 1.336(16) Å found in complexes **1**−**4**) (Table 1). The trends of RE−N, RE−O, and RE−C bond distances are in good agreement with the lanthanide contraction. The sum of the four angles of each amidate metallacycle is in the range from 358.0° to 359.9°, indicating no significant deviation from planarity (Table 1). This is similar to previously reported complexes.[25]

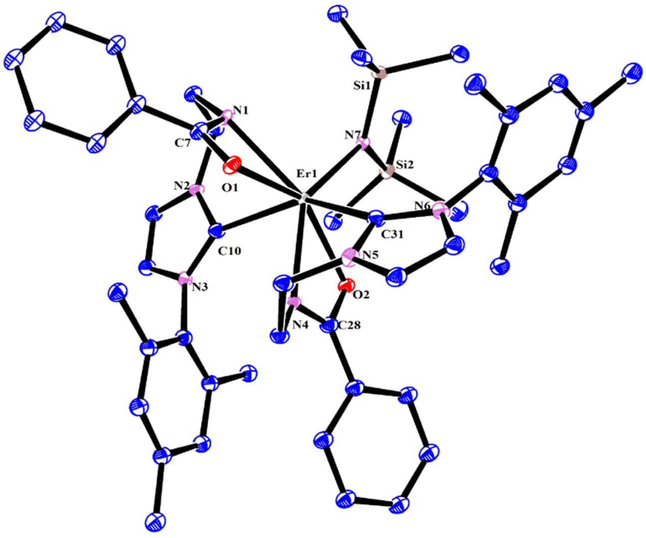


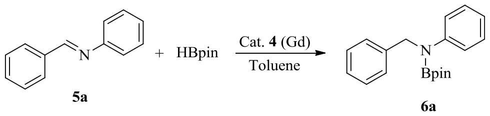
**Figure 1.** Ortep diagram of complex **1** with 15% probability thermal ellipsoids. The hydrogen atoms were omitted for clarity.

**Catalytic Hydroboration Reactions of Imines or Nitriles.** As discussed above, a few rare-earth metal complexes have been developed as catalysts for the hydroboration of imines or nitriles. With four catalysts **1**−**4** in hand, their catalytic activities were studied and compared in catalyzing the hydroboration of imines. *N*-Benzylideneaniline as a template substrate with pinacolborane (HBpin) was tested under various conditions. Initially, this reaction was performed using 1.5 equiv of HBpin in toluene in the presence of 2 mol % of catalyst **4** under argon at various temperatures for 24 h. As shown in Table 2, the desired hydroboration product **6a** was only obtained in 13% yield when the reaction was carried out at room temperature (entry 1); the yield of **6a** was improved to 82% yield when the reaction temperature was raised to 110 °C. Different ratios of the catalyst to HBpin were surveyed. If no catalyst was loaded, the yield of the product was no more than 10% (Table 2, entry 6). If the catalyst loading was only 1 mol %, the yield of the product declined to 75% (Table 2, entry 7). However, further increase of the catalyst loading (up to 5 mol %) brought only a slight increase of the yield of **6a** (up to 87%, Table 2, entries 8−9). Therefore, 2 mol % catalyst loading was used to achieve the optimized reaction conditions. The yield of the desired product **6a** was significantly decreased to 67% when the reaction time was shortened to 3 h, and only slight variation of the yield of product **6a** was observed when the reaction time was above 6 h (80−81%, Table 2, entries 11−12). Along with

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**−**4**

| | RE | | | |
|---|---|---|---|---|
| | Er (**1**) | Y (**2**) | Dy (**3**) | Gd (**4**) |
| RE(1)−N(1) | 2.462(7) | 2.471(5) | 2.484(7) | 2.524(9) |
| RE(1)−N(4) | 2.413(8) | 2.439(5) | 2.444(8) | 2.469(10) |
| RE(1)−O(1) | 2.371(7) | 2.375(4) | 2.404(7) | 2.430(9) |
| RE(1)−O(2) | 2.328(6) | 2.342(4) | 2.357(6) | 2.393(8) |
| RE(1)−C(10) | 2.618(9) | 2.640(6) | 2.645(8) | 2.678(10) |
| RE(1)−C(31) | 2.785(10) | 2.800(7) | 2.799(9) | 2.817(12) |
| O(1)−C(7) | 1.286(12) | 1.284(8) | 1.272(11) | 1.260(15) |
| O(2)−C(28) | 1.288(12) | 1.291(8) | 1.319(12) | 1.312(15) |
| C(7)−N(1) | 1.291(13) | 1.280(9) | 1.312(13) | 1.336(16) |
| C(28)−N(4) | 1.266(14) | 1.292(9) | 1.265(14) | 1.269(16) |
| C(10)−RE(1)−C(31) | 150.8(3) | 150.8(2) | 150.2(3) | 149.7(3) |
| RE(1)−O(1)−C(7) | 96.8(6) | 95.9(4) | 95.9(6) | 97.0(7) |
| RE(1)−O(2)−C(28) | 95.4(6) | 95.7(4) | 94.2(6) | 94.2(7) |
| O(1)−C(7)−N(1) | 115.3(9) | 117.1(6) | 119.1(9) | 117.5(11) |
| O(2)−C(28)−N(4) | 117.2(9) | 117.5(6) | 118.4(8) | 118.7(11) |
| C(7)−N(1)−RE(1) | 92.4(6) | 91.6(4) | 91.2(5) | 90.7(7) |
| C(28)−N(4)−RE(1) | 92.1(6) | 91.2(4) | 91.6(6) | 91.9(8) |
| N(1)−RE(1)−O(1) | 53.5(2) | 53.62(17) | 53.7(2) | 53.2(3) |
| N(4)−RE(1)−O(2) | 54.7(3) | 54.97(17) | 55.1(3) | 54.3(3) |

Table 2. Hydroboration of Imine: Optimization of Reaction Conditions[a]



| entries | Cat. 4 (mol %) | HBpin (mmol) | *V* (mL) | temp. (°C) | time (h) | yield of **6a** (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 2 | 1.5 | 3 | 23 | 24 | 13 |
| 2 | 2 | 1.5 | 3 | 60 | 24 | 26 |
| 3 | 2 | 1.5 | 3 | 90 | 24 | 61 |
| 4 | 2 | 1.5 | 3 | 100 | 24 | 70 |
| 5 | 2 | 1.5 | 3 | 110 | 24 | 82 |
| 6 | 0 | 1.5 | 3 | 110 | 24 | <10 |
| 7 | 1 | 1.5 | 3 | 110 | 24 | 75 |
| 8 | 3 | 1.5 | 3 | 110 | 24 | 83 |
| 9 | 5 | 1.5 | 3 | 110 | 24 | 87 |
| 10 | 2 | 1.5 | 3 | 110 | 3 | 67 |
| 11 | 2 | 1.5 | 3 | 110 | 6 | 80 |
| 12 | 2 | 1.5 | 3 | 110 | 12 | 81 |
| 13 | 2 | 1.5 | 2.0 | 110 | 6 | 83 |
| 14 | 2 | 1.5 | 1.0 | 110 | 6 | 87 |
| 15 | 2 | 1.5 | 0.5 | 110 | 6 | 95 |
| 16 | 2 | 1.0 | 0.5 | 110 | 6 | 81 |
| 17 | 2 | 1.2 | 0.5 | 110 | 6 | 88 |
| 18 | 2 | 2.0 | 0.5 | 110 | 6 | 96 |
| 19 | 2 | 2.5 | 0.5 | 110 | 6 | 96 |

[a] Charge order: [Cat.]-[solvent]-[HBpin]-[imine]. [b] Based on $^1H$ NMR (500 MHz) analysis of the reaction mixtures. Mesitylene was used as an internal standard.

the amount of solvent reduced to 0.5 mL, a 95% yield of product **6a** was observed (Table 2, entry 15). After that, we tried to change the loading of HBpin to see whether the yield of the product can be improved. When 1.2 equiv of HBpin was employed, the yield of the product dropped to 88% (Table 2, entry 17). The yield of the product was not significantly improved, whereas the loading of HBpin was further increased (Table 2, entries 18−19). Thus, the optimized conditions for the catalytic reaction were 2 mol % catalyst loading, and 1.5 equiv of HBpin in 0.5 mL toluene at 110 °C for 6 h.

The situ $^1H$ NMR monitoring of the reaction progress for the hydroboration of *N*-benzylideneaniline with HBpin in the presence of 2 mol % **2** indicated the first-order kinetic to *N*-benzylideneaniline (Figure 2), and the reaction can reach to completion in 6 h.

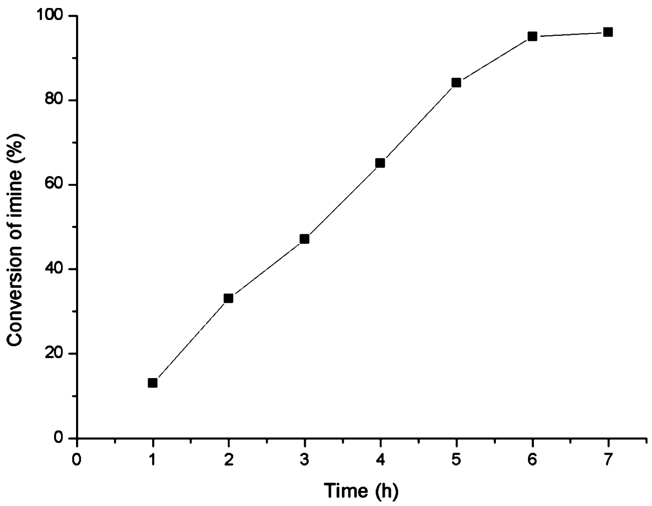


**Figure 2.** $^1H$ NMR monitoring of reaction progress: *N*-benzylideneaniline (0.1 mmol), HBpin (0.15 mmol), Cat. **2** (0.002 mmol), and $C_6D_6$ were charged in a screw-capped NMR tube. The reaction was monitored at regular intervals. The conversion was determined by integration of the proton of the imine *CH*═N in the $^1H$ NMR spectra.

Then, the catalytic activity of complexes **1**−**3** was investigated for the hydroboration of *N*-benzylideneaniline under optimized conditions. As summarized in Tables 2 and 3, these complexes displayed a comparably high catalytic performance for this hydroboration reaction. Other compounds such as $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, $Gd[N(SiMe_3)_2]_3$, and

Table 3. Hydroboration of Imine: Activity Comparison of Different of Complexes[a]

| entry | Cat. | yield of **6a** (%)[b] |
|---|---|---|
| 1 | Er (**1**) | 93 |
| 2 | Y (**2**) | 90 |
| 3 | Dy (**3**) | 92 |
| 4 | $NaN(SiMe_3)_2$ | 37 |
| 5 | $KN(SiMe_3)_2$ | 62 |
| 6 | $Gd[N(SiMe_3)_2]_3$ | 65 |
| 7 | $[(Me_3Si)_2N]_3Er(\mu\text{-}Cl)Li(THF)_3$ | 63 |
| 8 | $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ | 79 |
| 9 | $[(Me_3Si)_2N]_3Dy(\mu\text{-}Cl)Li(THF)_3$ | 78 |

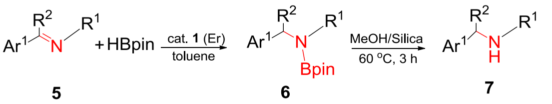
[a]Conditions: 2 mol % of Cat., 0.5 mL toluene, 1 mmol of *N*-benzylideneaniline, 1.5 mmol of HBpin, 110 °C. [b]Based on $^1H$ NMR (500 MHz) analysis of the reaction mixtures. Mesitylene was used as an internal standard.

$[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Er, Y, Dy) displayed moderate activity for the hydroboration reaction (Table 3, entries 4−9). These results indicated that the amidate-functionalized NHC ligand, which has a strong electron-donating carbene moiety, played an important role in the catalytic activity of the complexes.

Various imine substrates with different substitution patterns were then subjected to the hydroboration reaction in the presence of catalyst **1** under optimized conditions. In general, the reactions afforded the corresponding secondary amines in high to quantitative yield (82−99%) at 110 °C after a sequential work-up with methanol/silica (Table 4). The substituents with different electronic properties on either aromatic rings, such as alkyl groups (**5b** and **5c**), halogens (**5d**−**5h**), methoxy groups (**5i**, **5j**), naphthyl groups (**5m**), and even hydroxyl groups (**5k**) showed little influence on the yields of the products. Only the substrate with a strong electron-withdrawing $-NO_2$ group (**5l**) resulted in a relatively low yield of 50% with 1.5 equiv of HBpin, which could be improved to 82% by increasing the amount of HBpin to 3 equiv. The poor yield was probably due to its strong electron-withdrawing property which disfavors the coordination of the nitrogen of the imine to the metal center/or the chelation of the oxygen atoms of the nitro group with the metal center of the catalyst, which deferred the interaction of the imine C═N bond with the catalyst center. Furthermore, steric effects from the substituents also have a very limited effect on the yields. For example, substrates **5q**, **5w,** and **5x** with ortho substituents or sterically bulky groups also provided the corresponding products in high yields (85−95%).

The catalytic reactivity of complexes **1**−**4** has shown several notable advantages compared to other known catalytic systems. For example, the activity of these rare-earth metal complexes is apparently much higher than those of β-diketiminato magnesium alkyl {[CMe(NDipp)]CHMgR} (Dipp = diisopropylphenyl) and benzamidinato calcium $[PhC(N^iPr)_2CaI]$-based systems,[8b] where a relatively low activity toward imines (30−59%) was reported for the calcium catalyst, whereas for the magnesium catalyst, imine substrates such as **5q** could not be reduced even under harsh conditions (2% yield with 10 mol % [Mg] at 70 °C for 3 d vs 95% yield with 2 mol % [Er] at 110 °C for 6 h).[8b] It was reported that rhenium complex $[(PPh_3)_2Re(O)_2I]$ catalyzes the hydroboration of aldimines that are only derived from primary aliphatic amines, such as *N*-benzylidenemethanamine.[8c] Our catalysts are capable of catalyzing the hydroboration of imines derived from a broad range of aromatic amines with different functional groups, even those derived from bulky aliphatic primary amines (**7x** in Table 4). Ketimines were also subjected to the hydroboration conditions, which led to the hydroboration products in high yields (90 and 88% yield for **7y** and **7z**, respectively). The activity toward hydroboration of ketimine is comparable to that reported for systems using $BAr^F_3$ as the catalyst.[9e]

Table 4. Catalytic Hydroboration of Imines[a]



| entries | $Ar^1$ | $R^1$ | $R^2$ | product | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 4-MePh | Ph | H | **7b** | 95 |
| 2 | $3,4\text{-}Me_2Ph$ | Ph | H | **7c** | 96 |
| 3 | 4-FPh | Ph | H | **7d** | 95 |
| 4 | 2-FPh | Ph | H | **7e** | 99 |
| 5 | 4-ClPh | Ph | H | **7f** | 99 |
| 6 | 4-BrPh | Ph | H | **7g** | 94 |
| 7 | 4-IPh | Ph | H | **7h** | 94 |
| 8 | 4-MeOPh | Ph | H | **7i** | 98 |
| 9 | $3,4\text{-}(MeO)_2Ph$ | Ph | H | **7j** | 94 |
| 10 | 2-HOPh | Ph | H | **7k** | 97 |
| 11 | $4\text{-}O_2NPh$ | Ph | H | **7l** | 50 (82)[c] |
| 12 | 2-naphthyl | Ph | H | **7m** | 85 |
| 13 | Ph | $PhCH_2$ | H | **7n** | 87 |
| 14 | Ph | 4-MeOPh | H | **7o** | 99 |
| 15 | Ph | $4\text{-}^tBuPh$ | H | **7p** | 97 |
| 16 | Ph | $2,4,6\text{-}Me_3Ph$ | H | **7q** | 95 |
| 17 | Ph | $4\text{-}Me_2NPh$ | H | **7r** | 89 |
| 18 | Ph | $3\text{-}O_2NPh$ | H | **7s** | 62 (87)[c] |
| 19 | 4-MePh | 4-MePh | H | **7t** | 94 |
| 20 | 4-MeOPh | 4-MeOPh | H | **7u** | 95 |
| 21 | 4-ClPh | 4-ClPh | H | **7v** | 93 |
| 22 | 4-ClPh | 2-MePh | H | **7w** | 85 |
| 23 | 2-naphthyl | adamantyl | H | **7x** | 91 |
| 24 | 4-BrPh | Ph | Me | **7y** | 90 |
| 25 | 4-MeOPh | Ph | Me | **7z** | 88 |

[a]Conditions: 2 mol % of Cat., 0.5 mL toluene, 1 mmol of *N*-benzylideneaniline, 1.5 mmol of HBpin, 110 °C. [b]Isolated yield. [c]The data in parenthesis were obtained using 3 equiv of HBpin.

It was known that most catalysts that are active in the hydroboration of imine are generally less reactive for the nitriles.[8b] Inspired by the above catalytic activity of the complexes toward hydroboration of imines, we turned our attention to the catalytic hydroboration of the less active nitrile substrates with complexes **1**−**4**. 4-Methoxybenzonitrile was used as a model compound to investigate the catalytic performance of complexes **1**−**4** in the hydroboration of nitriles and to optimize the reaction condition (Table 5), after a simple survey of the catalytic reaction conditions (2 mol % of Cat. **1**, 1 mmol of nitrile, 3 mmol of HBpin, 0.5 mL toluene at temperature, 110 °C).

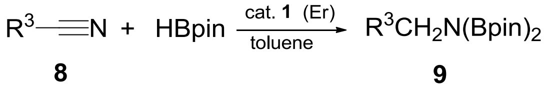
It is found that under optimized conditions (3 equiv of HBpin in the presence of 2 mol % of Cat. **1** at 110 °C), a broad range of nitriles, including both aromatic and aliphatic ones, were reduced to the corresponding dihydroborated products in excellent yields (89−99%) (Table 6). As was observed above in the hydroboration of imines, either the electronic property (**9d** vs **9e**) or the sterics (**9i**) of the substituents on the aromatic rings showed little effect on the yield of products. To the best of our

**Table 5. Hydroboration of 4-Methoxybenzonitrile with Different Complexes**[a]

| entry | Cat. | yield of **6a** (%)[b] |
|---|---|---|
| 1 | Er (**1**) | 96 |
| 2 | Y (**2**) | 95 |
| 3 | Dy (**3**) | 87 |
| 4 | Gd (**4**) | 93 |

[a]Conditions: 2 mol % of Cat., 0.5 mL toluene, 1 mmol of 4-methoxybenzonitrile, 3 mmol of HBpin, 110 °C. [b]Based on $^1H$ NMR (500 MHz) analysis of the reaction mixtures. Mesitylene was used as an internal standard.

**Table 6. Catalytic Hydroboration of Nitriles**[a]



$$R^3{-}C{\equiv}N + HBpin \xrightarrow[\text{toluene}]{\text{cat. } \mathbf{1} \text{ (Er)}} R^3CH_2N(Bpin)_2$$

**8** **9**

| entries | $R^3$ | product | yield (%)[b] |
|---|---|---|---|
| 1 | 4-MePh | **9a** | 93 |
| 2 | 4-FPh | **9b** | 96 |
| 3 | 3-MePh | **9c** | 99 |
| 4 | 4-$F_3$CPh | **9d** | 93 |
| 5 | 3-MeOPh | **9e** | 93 |
| 6 | 3-IPh | **9f** | 94 |
| 7 | 2-naphthyl | **9g** | 99 |
| 8 | 2-naphthyl$CH_2$ | **9h** | 89 |
| 9 | 2,4-$Cl_2$Ph | **9i** | 92 |
| 10 | 4-MeOPh | **9j** | 96 |
| 11 | 2-pyridine | **9k** | 93 |
| 12 | Et | **9l** | 97[c] |
| 13 | $^t$Bu | **9m** | 95[c] |

[a]Conditions: 2 mol % of Cat., 0.5 mL toluene, 1 mmol of nitrile, 3 mmol of HBpin, 110 °C. [b]Isolated yields. [c]Isolated as the corresponding ammonium salt.

knowledge, this represents the first example of rare-earth metal catalysts that are capable of efficiently catalyzing the hydroboration of both imines and nitriles.

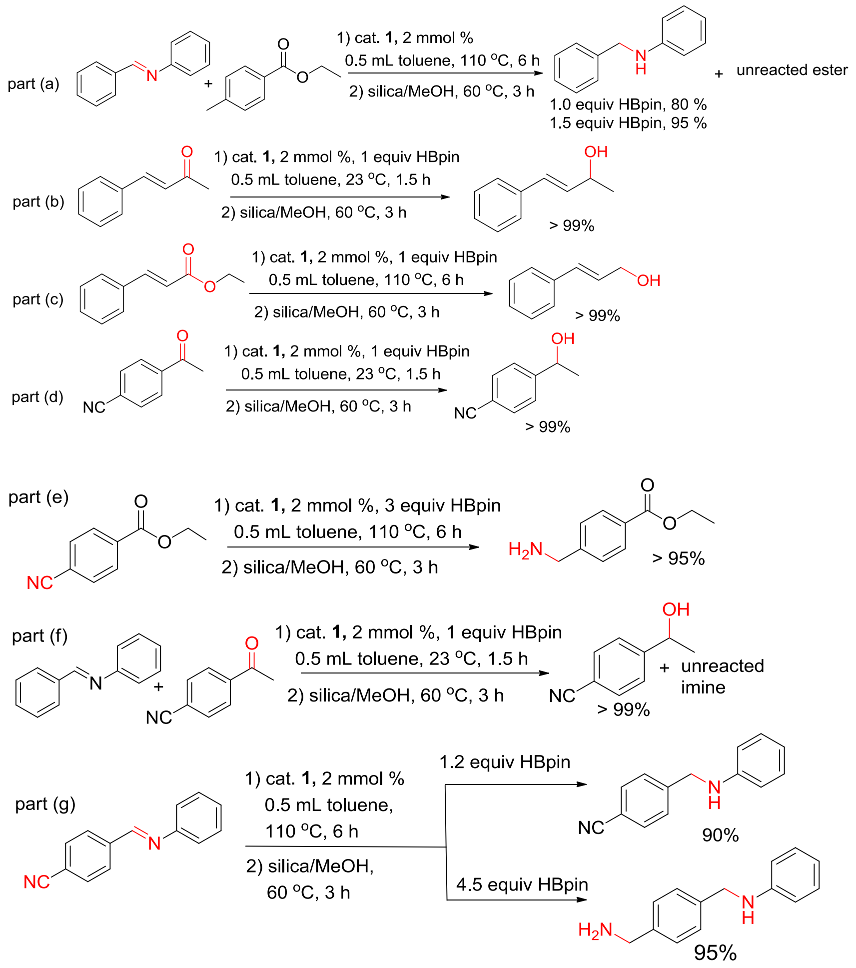
Because complexes **1**−**4** are efficient catalysts in both imine and nitrile hydroborations, it would be of great interest to study their selectivity in the reduction of substrates bearing a broader range of unsaturated functional groups. Competition reactions among the C═O, C═N, C≡N, $CO_2$Et, and C═C groups were tested using **1** as the catalyst (Scheme 2). Exclusive hydroboration of the imine was observed in the competition reaction between ethyl 4-methylbenzoate and *N*-benzylideneaniline [Scheme 2, part (a)], indicating that the imine was more reactive than the ester group under these conditions. When the benzalacetone bearing both C═C and C═O groups, or the ethyl cinnamate bearing both C═C and $CO_2$Et groups were subjected to the hydroboration conditions, selective hydroboration of the carbonyl group was completed after 1.5 h, whereas the ester group required 6 h to completion. In both cases, the C═C bonds were still intact [Scheme 2, part (b) and (c)], thus indicating a preference of C═O and $CO_2$Et reduction over the C═C bond reduction. The activity of **1** is comparable to the activities of the $La[N(SiMe_3)_2]_3$[16a] and tris(cyclopentadienyl)lanthanide complexes,[16b] but differs from that of a cobalt catalyst that catalyzes the reduction of olefins.[14a] When 4-acetylbenzonitrile was treated with 1 equiv of HBpin in the presence of complex **1**, the carbonyl group was again reduced completely in 1.5 h [Scheme 2, part (d)], whereas the treatment of ethyl 4-cyanobenzoate with 3 equiv of HBpin led to a reduction of the cyano group after 6 h [Scheme 2, part (e)], demonstrating the relative reactivity order of C═O > C≡N > $CO_2$Et. The reduction of the carbonyl group was found to be even faster than the imine group, as shown in the competitive hydroboration reaction between 4-acetylbenzonitrile and *N*-benzylideneaniline [Scheme 2, part (f)]. Lastly, it was found that for the substrates bearing both cyano and imine groups, the selective hydroboration of the imine was observed when only 1.2 equiv of HBpin was applied, producing the imine-reduced product in 90% yield. Increasing the amount of HBpin to 4.5 equiv eventually led to complete reduction of both imine and cyano groups, producing the corresponding product in 95% yield [Scheme 2, part (g)]. This result further highlighted that our rare-earth metal complexes **1**−**4** are highly active catalysts even for the reduction of the less reactive cyano group. In contrast, the previously mentioned benzamidinato calcium complex $[PhC(N^iPr)_2CaI]$ was completely inactive in the hydroboration of nitriles as the hydroboration of imines was performed in $CH_3CN$.[8b] Therefore, the catalysts **1**−**4** exhibited excellent chemoselectivity in the hydroboration of a variety of unsaturated groups, with the reactivity order as C═O ≫ C═N > C≡N > $CO_2$Et > C═C.

From previous work,[25] a possible mechanism for the hydroboration of imines is proposed (Scheme 3). The rare-earth metal hydride species was generated via the well-established σ-bond metathesis, which may exist as borohydride species **A** in the presence of excess pinacolborane[26c] (in ref 26c, a similar intermediate was proposed) and the inactive species **B**. The inactive species **B** was probed in the catalytic reaction with $^{11}B$ NMR spectra (see Figure S95 in the Supporting Information). The intermediate **A** can be observed by probing the reaction of the amido complex **2** with HBpin in $C_6D_6$ showing a weak resonance at ~3.3 ppm (see Figure S96 in the Supporting Information). The σ-metathesis reaction product $TMS_2$NBpin was observed in the $^{13}C$ NMR probing reaction of catalyst **2** with HBpin (See Figure S97 in the Supporting Information). The compound $TMS_2$NBpin was also isolated and characterized (see Figures S98−100 in the Supporting Information). In the presence of an amine substrate, the borohydride species **A** may dissociate into the active hydride species that undergoes the imine C═N bond insertion to form the amido intermediate. The latter then reacts with another molecule of HBpin to release the product and regenerate the active hydride to accomplish the catalytic cycle. In the case of nitrile hydroboration, two sequential steps involving an intermediate RCH═NBpin can be proposed.[10,11c,12c,13a] Thermal decomposition or disproportionation of HBpin to $BH_3$ was excluded because heating HBpin with or without the rare-earth metal complex under 110 °C did not result in any changes in the $^{11}B$ NMR spectrum, and the formation of free $BH_3$ was not observed under this condition, which may exclude the possible reduction caused by $BH_3$ under the catalyzed or noncatalyzed process.[16a,26c,d]

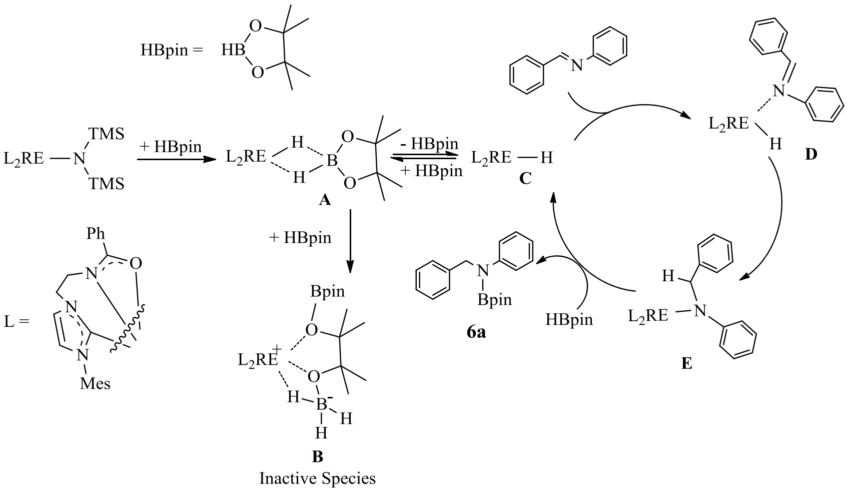
## ■ CONCLUSIONS

In summary, a series of rare-earth metal amido complexes bearing amidate-functionalized NHC ligands were synthesized and characterized. The complexes exhibited a high catalytic activity toward hydroboration of both imines and nitriles, which represents the first examples of rare-earth metal complexes as catalysts capable of catalyzing the hydroboration of both imines and nitriles. These catalysts have shown several notable features

**Scheme 2. Chemoselective Hydroboration of Unsaturated Compounds**



**Scheme 3. Proposed Mechanism for the Hydroboration of Imines**



compared to other reported systems, including high catalytic efficiency, relatively low catalyst loading, and a wide functional group tolerance, thus providing a general catalytic method for the synthesis of primary and secondary amines. The notable chemoselectivity exhibited by these catalysts may also find their further application in the synthesis of more complex and valuable products.

## ■ EXPERIMENTAL SECTION

**General Considerations.** All operations were performed under an argon atmosphere, using the standard Schlenk-line or glovebox technique. $KN(SiMe_3)_2$ and nitriles were commercially available and used as received. THF, toluene, and *n*-hexane were dried and free of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. Imines and the anhydrous $RECl_3$ (RE = Er, Y, Dy, Gd) were synthesized according to the literature-reported procedures.[27] Amidate functionalization imidazole salt was synthesized as the methods described in the literature.[24] NMR spectra were recorded on a Bruker model AV-300 spectrometer, Bruker model AV-400 spectrometer, or Bruker model AV-500 spectrometer in $C_6D_6$, $D_2O$, or $CDCl_3$. Elemental analysis was performed on a Vario EL III elemental analyzer. Single-crystal data were performed on a Bruker Smart APEX II charge-coupled device single-crystal X-ray diffractometer. Melting points were observed in sealed capillaries. IR spectra were performed on a Shimadzu model FTIR-8400s spectrometer. HRMS were measured on an Agilent model 6220-TOF mass spectrometer.

**Synthesis of (1-(2-Benzamido)-ethylene-3-mesityl)-imidazolium Bromide ($H_2LBr$) (1-($C_6H_5C{=}ONHCH_2CH_2$)-3-$(CH_3)_3C_6H_2$-$(N(CH)_2NCH)$)Br ($H_2LBr$).** To a 500 mL round-bottom flask containing 200 mL acetonitrile was added *N*-(2-bromoethyl)-benzamide (22.8 g, 100 mmol) and 1-mesityl imidazole (18.6 g, 100 mmol). The mixture was refluxed for 12 h. The product precipitated from the reaction mixture and was collected by filtration. The proligand $H_2LBr$ was well characterized by spectroscopic methods. Yield: 40.6 g, 98%. mp 220.6 °C. IR (KBr pellets, $cm^{-1}$) $\nu$: 3211, 3055, 2359, 1638, 1578, 1545, 1495, 1450, 1300, 1215, 1200, 1161, 1115, 845, 831, 704, 664, 619, 571. $^1H$ NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ 9.96 (s, 1H, NC*H*N), 9.27 (t, 1H, *J* = 5.5 Hz, NH), 8.07 (d, 2H, *J* = 7.5 Hz), 7.97 (s, 1H), 7.40 (t, 1H, *J* = 7 Hz), 7.33 (t, 2H, *J* = 8 Hz), 7.02 (s, 1H), 6.84 (s, 2H), 5.08 (t, 2H, *J* = 5 Hz), 4.08 (t, 2H, *J* = 5.5 Hz), 2.24 (s, 3H, $CH_3$), 1.76 (s, 6H, $CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$, 298 K): $\delta$ 168.1 (*C*=O), 141.7 (*p*-Mes-C), 138.5 (NCN), 134.6 (*o*-Mes-C), 133.1 (*p*-Mes-C), 132.0 (*i*-Mes-C), 130.9 (*i*-Ph-C), 130.1 (*m*-Mes-CH), 128.7 (*o*-Ph-CH), 128.2 (*m*-Ph-CH), 124.0 (CH), 123.4 (CH), 49.4 ($NCH_2$), 39.4 ($NHCH_2$), 21.4 (*p*-Mes-$CH_3$), 17.5 (*o*-Mes-$CH_3$). HR-MS (APCI) *m*/*z*: calcd for $C_{21}H_{24}N_3O$ $[M - Br]^+$, 334.1914; found, 334.1920.

**Synthesis of $[(\kappa^2\text{-N,O-}\kappa^1\text{-L})_2ErN(SiMe_3)_2]$ (1).** To a suspension of $ErCl_3$ (273 mg, 1.0 mmol) and imidazolium salt (**$H_2LBr$**, 828 mg 2.0 mmol) in 15 mL THF was added a THF solution of KHMDS (5.0 mL, 5.0 mmol) slowly at −40 °C. The reaction mixture was gradually warmed to room temperature and stirred for 6 h. All volatiles were removed under reduced pressure, and the residues were recrystallized from a mixture of THF and *n*-hexane to afford **1** as pink crystals. Yield: 347 mg, 35%. mp 122.8 °C. IR (KBr pellets, $cm^{-1}$) $\nu$: 3051, 2358, 1645, 1533, 1489, 1447, 1364, 1294, 1200, 1161, 1096, 1069, 1022, 934, 853, 714, 698, 669. Anal. Calcd for $C_{48}H_{62}N_7O_2Si_2Er(C_4H_8O)_2$: C, 59.17; H, 6.92; N, 8.63. Found: C, 58.97; H, 6.85; N, 8.59.

**Synthesis of $[(\kappa^2\text{-N,O-}\kappa^1\text{-L})_2YN(SiMe_3)_2]$ (2).** A similar procedure to that for the preparation of complex **1** was used. Complex **2** crystallized from a mixture of THF and *n*-hexane. Yield: 274 mg, 30%. mp 134.8 °C. $^1H$ NMR (500 MHz, $C_6D_6$, 298 K): $\delta$ 7.32 (s, 3H), 7.14 (t, 7H), 6.63 (s, 3H), 5.98 (d, 2H), 5.89 (s, 2H), 3.54–3.53 (m, 8H), 2.09 (s, 12H, C*H*$_3$), 1.99 (s, 6H, C*H*$_3$), 0.39 (s, 18H, Si(C*H*$_3$)$_3$). $^{13}C$ NMR (125 MHz, $C_6D_6$, 298 K): $\delta$ 197.3, 197.1, 177.4, 137.9, 137.4, 135.7, 129.5, 129.2, 128.4, 127.4, 120.7, 120.6, 67.8, 52.5, 48.9, 25.8, 21.2, 18.9, 6.2, 2.7. IR (KBr pellets, $cm^{-1}$) $\nu$: 3057, 2349, 1645, 1531, 1487, 1402, 1296, 1250, 1202, 1161, 1070, 1022, 934, 851, 714, 671, 419. Anal. Calcd for $C_{48}H_{62}N_7O_2Si_2Y(C_4H_8O)$: C, 63.33; H, 7.15; N, 9.94. Found: C, 62.90; H, 7.26; N, 9.70.

**Synthesis of $[(\kappa^2\text{-N,O-}\kappa^1\text{-L})_2DyN(SiMe_3)_2]$ (3).** A similar procedure to that for the preparation of complex **1** was used. Complex **3** crystallized from a mixture of THF and *n*-hexane. Yield: 325 mg, 33%. mp 123.8 °C. IR (KBr pellets, $cm^{-1}$) $\nu$: 3053, 2355, 1655, 1539, 1489, 1449, 1366, 1306, 1250, 1202, 1161, 1092, 1070, 1022, 934, 839, 710, 577. Anal. Calcd for $C_{48}H_{62}N_7O_2Si_2Dy(C_4H_8O)$: C, 58.93; H, 6.66; N, 9.25. Found: C, 58.79; H, 6.68; N, 9.04.

**Synthesis of $[(\kappa^2\text{-N,O-}\kappa^1\text{-L})_2GdN(SiMe_3)_2]$ (4).** A similar procedure to that for the preparation of complex **1** was used. Complex **4** crystallized from a mixture of THF and *n*-hexane. Yield: 442 mg, 45%. mp 119.9 °C. IR (KBr pellets, $cm^{-1}$) $\nu$: 3031, 2351, 1645, 1601, 1568, 1557, 1487, 1427, 1373, 1348, 1306, 1290, 1258, 1119, 1059, 932, 839, 756, 692. Anal. Calcd for $C_{48}H_{62}N_7O_2Si_2Gd(C_4H_8O)_2$: C, 59.70; H, 6.98; N, 8.70. Found: C, 59.53; H, 7.09; N, 8.76.

**General Catalytic Process for the Hydroboration of Imines.** Catalyst **2** (2 mol %), 0.5 mL toluene, HBpin (217 $\mu$L, 1.5 mmol), and imine (1 mmol) were charged in a Schlenk tube in the glovebox. The reaction mixture was allowed to stir at 110 °C for 6 h. The reaction mixture was monitored by the $^1H$ NMR technique with integration relative to mesitylene and appearance of new $CH_2$ resonance signals. Upon completion, the reaction mixture was treated with silica gel and methanol at 60 °C for 3 h. The reaction mixtures were purified by column chromatography with ethyl acetate/petroleum ether (v/v = 1:5) to provide the pure secondary amines.

***N*-benzylaniline (7a).** Light yellow oil. Yield 168 mg, 95%. IR (DCM, KBr pellets, $cm^{-1}$) $\nu$: 3418, 3051, 3026, 2841, 1601, 1506, 1452, 1325, 1267, 1252, 750, 731, 692. $^1H$ NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ 7.38 (d, 2H, *J* = 7.5 Hz), 7.35 (t, 2H, *J* = 7.5 Hz), 7.29 (d, 1H, *J* = 7 Hz), 7.18 (t, 2H, *J* = 7.5 Hz), 6.72 (t, 1H, *J* = 7.5 Hz), 6.64 (d, 2H, *J* = 8 Hz), 4.33 (s, 2H, C*H*$_2$), 4.03 (s, 1H, N*H*). $^{13}C$ NMR (125 MHz, $CDCl_3$, 298 K): $\delta$ 148.7, 140.0, 129.8, 129.2, 128.0, 127.7, 118.1, 113.4, 48.8. HR-MS (APCI) *m*/*z*: calcd for $C_{13}H_{14}N$ $[M + H]^+$, 184.1121; found, 184.1117.

Data for **7b**−**7z**, see the Supporting Information.

**General Catalytic Process for the Hydroboration of Nitriles.** Catalyst **2** (2 mol %), 0.5 mL toluene, HBpin (435 $\mu$L, 3 mmol), and nitrile (1 mmol) were charged a Schlenk tube in the glovebox. The reaction mixture was allowed to stir at 110 °C for 6 h. The reaction mixture was monitored by the $^1H$ NMR technique with integration relative to mesitylene and appearance of new $CH_2$ resonance signals. After work-up, the product was dried under vacuum.

**4,4,5,5-Tetramethyl-*N*-(4-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (9a).** IR (KBr pellets, $cm^{-1}$) $\nu$: 3096, 2994, 2978, 2930, 2097, 1624, 1566, 1477, 1443, 1385, 1360, 1177, 1126, 1067, 941. $^1H$ NMR (500 MHz, $CDCl_3$, 298 K): $\delta$ 7.22 (d, 2H, Ph*H*), 7.06 (d, 2H, Ph*H*), 4.21 (s, 2H, C*H*$_2$), 2.31 (s, 3H, C*H*$_3$), 1.21 (s, 24H, C*H*$_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$, 298 K): $\delta$ 140.5, 135.8, 128.9, 127.8, 82.7, 47.3, 24.9, 21.5. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K): $\delta$ 26.1 (s, B−N). HR-MS (APCI) *m*/*z*: calcd for $C_8H_{11}N$ $[M - C_{12}H_{21}B_2O_4]^+$, 122.0964; found, 122.0959.

Data for **9b**−**9m**, see the Supporting Information.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02067.

> Crystallographic details for complexes **1**−**4**, and crystal data were deposited in Cambridge Crystal Data Centre with CCDC 1575083−1575086 (PDF)

### Accession Codes

CCDC 1575083−1575086 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.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support for this work was provided by the National Natural Science Foundation of China (21432001, 21871004, and 21202002), the grants from Anhui Province (2017D107), and the Special and Excellent Research Fund of Anhui Normal University.

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DOI: 10.1021/acs.inorgchem.8b02067