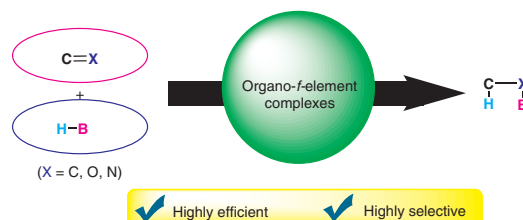


# Organo-*f*-Complexes for Efficient and Selective Hydroborations

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**Abstract** Organo-*f*-complexes catalyzing small molecule transformations have been a hot topic in the past few years. Compared to other transformations, the hydroboration of C=X (X = C, N, O) unsaturated bonds serves as an important strategy to prepare organoborane derivatives, which are important intermediates in organic synthesis. This review outlines recent advances in organolanthanide and organoactinide complexes promoting the hydroboration of C=X containing substrates. After a brief introduction, three types of hydroboration will be presented: alkene hydroboration, carbonyl hydroboration, and imine and nitrile hydroborations. The catalytic performance, mechanism, and kinetic studies are discussed in detail, aiming to emphasize the catalytic differences between the diverse organo-*f*-catalysts. Additionally, challenges and future directions of this field are also presented.

- 1 Introduction
- 2 Alkene Hydroboration
- 3 Carbonyl Hydroboration
- 4 Imine and Nitrile Hydroboration
- 5 Conclusions and Outlook

**Keywords** organolanthanide, organoactinide, hydroboration, selective, alkene, imine, ketone, aldehyde

## 1 Introduction

Organo-*f*-element complex, including organolanthanides and organoactinides, catalyzed small molecule transformations have experienced colossal acceleration in research activity in the past few years.<sup>1</sup> The unique advantages of organo-*f*-element complexes, versus other main group, transition-metal complexes, lies in the presence of the *f* orbitals and large ionic radii, which leads to large coordination numbers, large and flexible coordination geometries, high Lewis acidity, and thereof distinctive catalytic behaviors.<sup>2</sup>

The catalytic performances of organo-*f*-element complexes in organic transformations are significantly influenced by the nature of metal ions and the steric and electronic effects of the ancillary ligands. For instance, for the majority of organolanthanide-promoted hydroelementations, larger metal ions bearing more sterically opening coordination spheres generally demonstrate higher activity than smaller counterparts,<sup>3</sup> therefore, the reactivities of organolanthanides can be easily fine-tuned according to the rule of the lanthanide contraction.<sup>4</sup> Moreover, lanthanides and early actinide (Th) exhibit predominantly one oxidation state (+3 and +4 respectively), excluding conventional oxidative addition/reductive elimination pathways, which is very common in transition-metal complexes.<sup>5</sup> Olefin-insertion and  $\sigma$ -bond metathesis are the two most general reactive patterns for organolanthanide- and organoactinide-promoted transformations.<sup>4a</sup>

Due to the highly oxophilic nature of the lanthanide and actinide centers, when reacting with oxygen-containing substrates, thermodynamically stable and catalytically inactive Ln–O and An–O bonds are preferably formed, making the transformation of these substrates extremely challenging.<sup>5,6</sup> Therefore, despite the tremendous advances that we have witnessed in small molecule transformations, only a few of them have involved oxygen-containing substrates. Partially, for the same reason, organolanthanide- and organoactinide-catalyzed hydroboration have undergone a renaissance only in recent years due to the presence of oxygen atoms in some borane agents, such as catecholborane and pinacolborane.

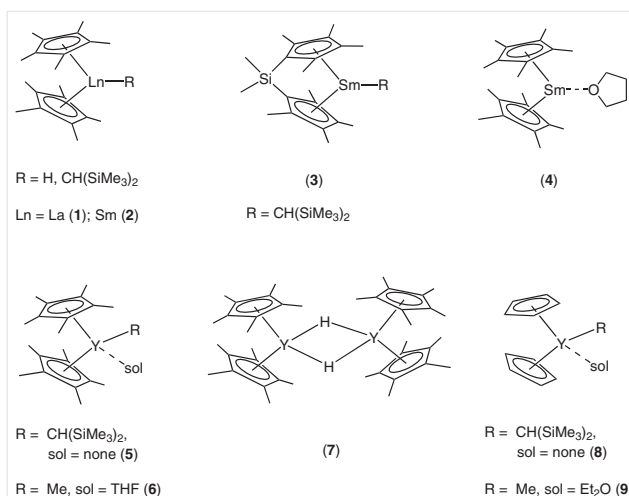
Organoboranes are a class of vital organic intermediates in a variety of organic transformations, and hydroboration of unsaturated bonds serves as a powerful strategy in preparing organoboranes.<sup>7</sup> Ever since the milestone discovery of the hydroboration of the C=C bond by Brown and co-workers,<sup>8</sup> rapid development and continuous momentum

has been gained in this area. Diversified main group metal catalysts ( $\text{Li}$ ,<sup>9</sup>  $\text{K}$ ,<sup>10</sup>  $\text{Mg}$ ,<sup>11</sup>  $\text{Al}$ ,<sup>12</sup>  $\text{Zn}$ ,<sup>13</sup>), transition-metal catalysts ( $\text{Ti}$ ,<sup>14</sup>  $\text{Co}$ ,<sup>15</sup>  $\text{Ni}$ ,<sup>16</sup>  $\text{Fe}$ ,<sup>17</sup>  $\text{Pd}$ ,<sup>18</sup>  $\text{Cu}$ ,<sup>19</sup>  $\text{Rh}$ ,<sup>20</sup>  $\text{Ir}$ ,<sup>21</sup>  $\text{Ag}$ ,<sup>22</sup>), organocatalysts,<sup>23</sup> and even catalyst-free systems,<sup>24</sup> etc., were designed to efficiently and selectively promote hydroborations of unsaturated bonds. Reviews or chapters on the hydroboration of unsaturated bonds have been systematically compiled previously,<sup>25</sup> whereas few of them addressed organolanthanide and organoactinide systems, despite their indispensable significance in this field.

Hence, in this review, we will concentrate on recent advances in organolanthanide- and organoactinide-mediated hydroboration reactions. We mainly focus on three types of hydroborations, i.e. alkene hydroboration, carbonyl hydroboration, and imine and nitrile hydroboration, and we draw some conclusions on the challenges and future development directions of this field.

## 2 Alkene Hydroboration

Organo-*f*-complex mediated hydroboration reactions were firstly reported by the Marks group in 1992.<sup>26</sup> In this report, cyclopentadienyl lanthanum and samarium complexes **1–4** (Figure 1) catalyzed the hydroboration using catecholborane as the borating agent, and the use of different types of alkenes was demonstrated. In the presence of a 25–100-fold excess of hex-1-ene, complex **1** exhibits an efficient catalytic rate ( $\text{TOF} \approx 200 \text{ h}^{-1}$ ), selectively affording the *anti*-Markovnikov product, hexan-1-ol, after the oxida-



**Figure 1** Organolanthanide complexes **1–9** for alkene hydroborations

tive workup (Scheme 1). Subsequent studies on various alkene substrates showed that the reaction rate followed the order of terminal alkene  $\geq$  terminal disubstituted alkene  $>$  internal disubstituted alkene  $>$  internal trisubstituted alkene, and no reaction was detected for the tetra-substituted substrate, 2,3-dimethylbut-2-ene. Similar to other organolanthanide-catalyzed small molecule transformations,<sup>27</sup> this phenomenon is likely caused by the steric demands at the metal center, i.e. sterically less congested substrates are more easily accessible to the active species. For the same reason, both larger metal ions and more

### Biographical Sketches



**Heng Liu** obtained his B.Eng. degree in polymer material and engineering from Nanchang University in 2009, and Ph.D. in polymer chemistry and physics from Changchun Institute of Applied Chemistry, Chinese Academy of Science. In 2015, he

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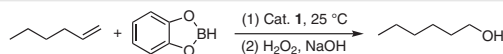


**Moris S. Eisen** immigrated to Israel in 1977 from Colombia. He received his Ph.D. from the Hebrew University in Jerusalem under the supervision of Prof. Jochanan Blum. In 1990 as a Weizmann Postdoctoral Fellow, he joined Prof. Tobin J. Marks'

group at Northwestern University. In 1992 he was awarded the State of Israel Alon Fellowship and joined the Department of Chemistry at the Technion-Israel Institute of Technology (since 2007, Schulich Faculty of Chemistry). Since 2003, he is a

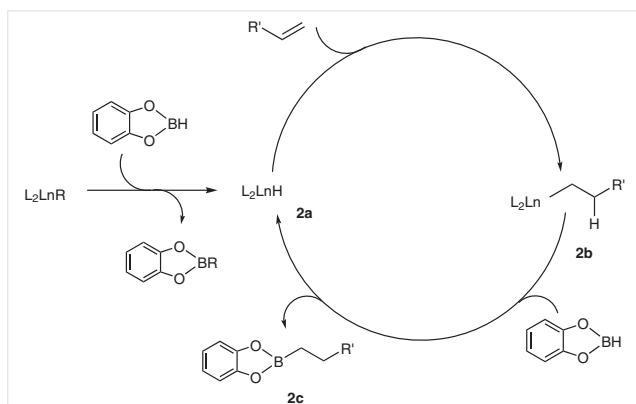
Full Professor and has served from 2004 as the Head of the Institute of Catalysis Science and Technology at the Technion. He is incumbent of the Samuel O. Friedlander Academic Chair in Chemistry.

sterically opening ligation were able to increase the hydroboration rate significantly. For instance, the reaction rate of complex **1** is 10-fold greater than that of complex **2**, and complex **3** is fourfold as active as complex **2**. The readily accessible samarium complex **4** also promoted the hydroboration process efficiently.



**Scheme 1** Hydroboration of hex-1-ene by complex **1**

The catalytic mechanism proposed by the Marks group is presented in Scheme 2. In the first activation step, the protonolysis of the lanthanide alkyl catalyst with catecholborane generates the active species, lanthanide hydride **2a**, which is followed by the insertion of an olefin in an *anti*-Markovnikov manner to form complex **2b**. Subsequent  $\sigma$ -bond metathesis with another molecule of catecholborane gives the final product, the boronate ester **2c**, and simultaneously regenerates the lanthanide hydride.

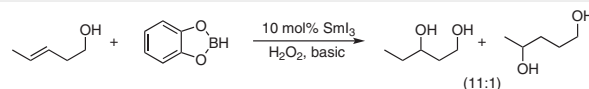


**Scheme 2** Proposed mechanism for organolanthanide-catalyzed olefin hydroboration

Following this pioneering research, the Evans group extended the catalyst categories beyond lanthanide cyclopentadienyl complexes.<sup>28</sup> They successfully demonstrated that ancillary ligands were not strictly required for the hydroboration process. For the hydroboration reaction of dec-1-ene with catecholborane, samarium triiodide ( $\text{SmI}_3$ ), diiodo-samarium *tert*-butoxide [ $(t\text{-BuO})\text{SmI}_2$ ], and the homoleptic samarium isopropoxide [ $(i\text{PrO})_3\text{Sm}$ ], were all found to be efficient catalysts, affording decan-1-ol in good yields after oxidation with hydrogen peroxide, whereas  $\text{SmBr}_3$ ,  $\text{SmCl}_3$ ,  $\text{SmF}_3$ , and  $\text{Sm}(\text{OTf})_3$  were inactive. Other trivalent group 3 and lanthanide salts, including  $\text{ScI}_3$ ,  $\text{PrI}_3$ ,  $\text{LuI}_3$ , also displayed good activities towards the hydroboration process. Subsequent studies of the scope of the reaction revealed that mono-, di-, and trisubstituted alkene substrates could efficiently undergo hydroboration when being catalyzed by 10 mol%  $\text{SmI}_3$ . For styrenic substrates, primary alcohol prod-

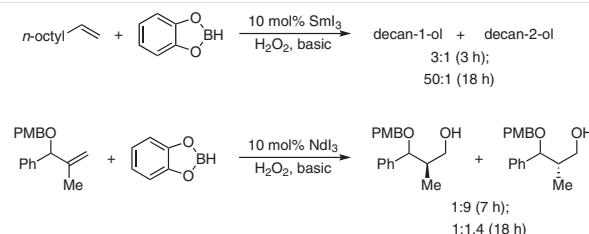
ucts, i.e. *anti*-Markovnikov products, resulted predominately; trisubstituted olefins, such as phenylcyclohexene and  $\alpha$ -pinene, gave exclusively *cis*-addition products.

The possibility of the hydroboration of functionalized olefins was also explored. In the presence of 10 mol%  $\text{SmI}_3$ , pent-3-en-1-ol was hydroborated with catecholborane in 73% yield, giving the two diol isomers in an 11:1 ratio (Scheme 3).



**Scheme 3** Hydroboration of pent-3-en-1-ol by  $\text{SmI}_3$

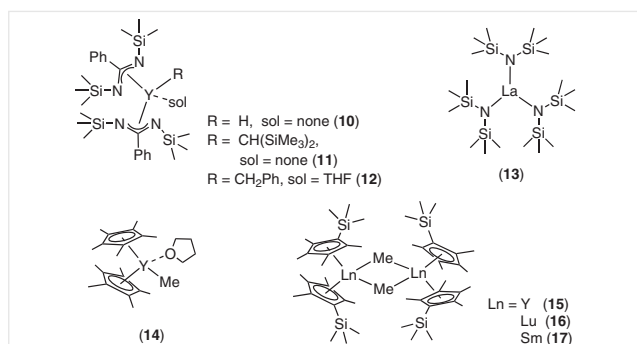
Moreover, the regioselectivity of this  $\text{SmI}_3$ -promoted hydroboration was discovered to be time dependent. For dec-1-ene hydroboration (Scheme 4, top), extending the reaction time from 3 hours to 18 hours resulted in a change of the ratio of the two products, decan-1-ol and decan-2-ol, from 3:1 to 50:1. A similar phenomenon was also reflected in the diastereoselectivity of two alcohol enantiomers (Scheme 4, bottom). These results can be explained by the isomerization towards the kinetically favored boronate esters with prolonged reaction times.



**Scheme 4** Time-dependent selectivity for lanthanide-catalyzed hydroborations

The Teuben group systematically explored the catalytic behaviors of a family of cyclopentadienyl and benzamidinate lanthanide complexes towards the hydroboration of hex-1-ene.<sup>29</sup> It was found that yttrocene complexes displayed much lower catalytic activities than their lanthanocene counterparts because of the smaller atom radius and thereof increased  $\sigma$ -bond metathesis transition state energy (formation of the hydroboration product and regeneration of metal hydride is the rate-determining step). For instance, complex **5** was found to be less active than complex **1** under identical conditions. This conclusion is in line with Marks's previous hydroboration observations and other lanthanide-catalyst-promoted catalytic transformations.<sup>26</sup> Changing the metal attached alkyl substituents from bis(trimethylsilyl)methyl (**5**) to methyl (**6**) and hydride (**7**) gave similar results to complex **5**. Employing sterically less congested yttrocene complexes, **8** and **9**, revealed remarkable increases in catalytic activities.

Besides cyclopentadienyl complexes, benzamidinate yttrium counterparts were also investigated by the Teuben group, based on the consideration that this type of ligand is a 'harder' Lewis base, which will have a strong influence on the transition state of the final  $\sigma$ -bond metathesis rate-determining step. Furthermore, the steric bulkiness of benzamidinate ligands is presumed to be between that of the cyclopentadienyl and pentamethylcyclopentadienyl ligands, which favors building the relationship between steric hindrance and catalytic performances. Through the catalytic results, it was revealed that all benzamidinate complexes are active in the hydroboration process, but their activities are roughly 1/30 to 1/12 of that of the lanthanocene complex **1**. Complexes **10** and **11** (Figure 2) showed catalytic activities substantially higher than **5–7**, but lower than **8** and **9**, which is in accordance with the steric characteristics. When Lewis bases are present in the complex, such as THF in **12**, rapid decomposition of catecholborane to bis(pinacolato)diboron dimer is detected.

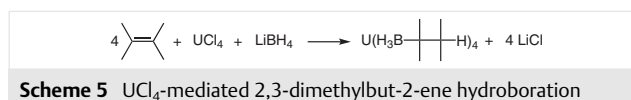


**Figure 2** Organolanthanide complexes **10–17** for alkene hydroborations

Livinghouse and co-workers, carried out alkene-pinacolborane hydroborations using commercially available tris[bis(trimethylsilyl)amide]lanthanum (**13**) and cyclopentadienyl yttrium **14** complexes.<sup>30</sup> In the presence of 3 mol% of **13**, hex-1-ene was hydroborated by pinacolborane (HBpin) giving hexan-1-ol in 90% isolated yield, which is significantly superior to that obtained using complex **14** under identical conditions. The hydroboration was also highly efficient for other alkene substrates, including cyclohexene, indene, styrenic monomers, all of which proceeded to >99% conversions and revealed *anti*-Markovnikov selectivity. It is of note that the introduction of strong electron-withdrawing or -donating *para* substituents to styrenic substrates had little influence on the catalytic behaviors, both types of compounds were catalyzed rapidly under mild conditions.

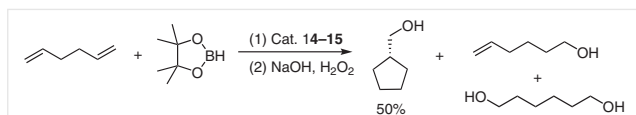
Due to steric influences, the reactivity of alkene substrates in hydroboration transformations usually follows the order of mono- > di- > tri- > tetrasubstituted C=C bonds. However, Villiers and Ephritikhine found that in the presence of  $\text{UCl}_4$  or  $\text{NdCl}_3$  the hydroboration of alkenes with  $\text{LiBH}_4$  followed the completely opposite order to that in pre-

vious reports.<sup>31</sup> Treating 2,3-dimethylbut-2-ene with  $\text{LiBH}_4$  and  $\text{UCl}_4$  gave uranium alkylborohydride in high yield (90%), which immediately gave 2,3-dimethylbutan-2-ol upon oxidation by alkaline hydrogen peroxide (Scheme 5). Trisubstituted alkenes, such as  $\alpha$ -pinene, 2-methylpent-2-ene, etc., were less reactive than 2,3-dimethylbut-2-ene and the reactions required a longer time to reach completion. Most striking is that less substituted alkenes (cyclohexene, 2-methylpropene, and hex-1-ene) were found to be inert towards the hydroboration process, which completely disobeys the general rule concluded previously.  $\text{NdCl}_3$  was also found to demonstrate similar results, but with slower reactivities.

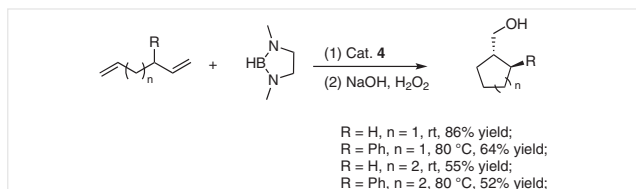


Inspired by lanthanocene-mediated cyclization/silylation of 1,1-disubstituted dienes for the preparation of functionalization carbocycles, Molander and Pfeiffer reported the first examples of an organolanthanide-catalyzed cyclization/boration reaction of 1,5- and 1,6-dienes to give primary cyclic alcohols.<sup>32</sup> Initially they examined the reaction between hexa-1,5-diene and catecholborane catalyzed by complex **4**, which proved ineffective. Changing to other lanthanide metallocene complexes **14** and **15** and using HBpin as the hydroboration reagent gave the desired cyclized cyclopentylmethanol in yields up to 50%, but with many byproducts, such as hex-5-en-1-ol and hexane-1,6-diol, which came from  $\sigma$ -bond metathesis in an undesired uncyclized hydroboration fashion (Scheme 6). In order to slow down  $\sigma$ -bond metathesis and simultaneously promote the cyclization reaction, the reaction of 1,3-dimethyl-1,3-diaza-2-boracyclopentane (1,3-dimethyl-1,3,2-diazaborolidine) with hexa-1,5-diene was examined in the presence of complex **4**, and it then proved to be an efficient and selective hydroboration reagent affording the cyclic alcohol product in 86% yield (Scheme 7,  $R = \text{H}$ ,  $n = 1$ ). Whereas, the yttrocene complex **14** did not show any activity in this reaction perhaps due to the smaller metal ionic radius as concluded above. Increasing the steric effects on the ancillary cyclopentadienyl ligands by using complexes **15–17** (Figure 2), the desired products were obtained in yields ranging from 40% for  $\text{Ln} = \text{Lu}$  (**16**) to 62% for  $\text{Ln} = \text{Y}$  (**15**), and 74% for  $\text{Ln} = \text{Sm}$  (**17**). The use of other substituted 1,5- and 1,6-dienes was also feasible in this cyclization/boration reaction, but the formation of six-membered rings is comparatively less efficient than the formation of five-membered rings (Scheme 7).

The proposed mechanism for the cyclization/boration reaction is presented in Scheme 8. The precatalyst firstly reacts with the organoborane to generate the catalytically active species lanthanide hydride **8a**, which then regioselectively inserts into one of the terminal double bonds to

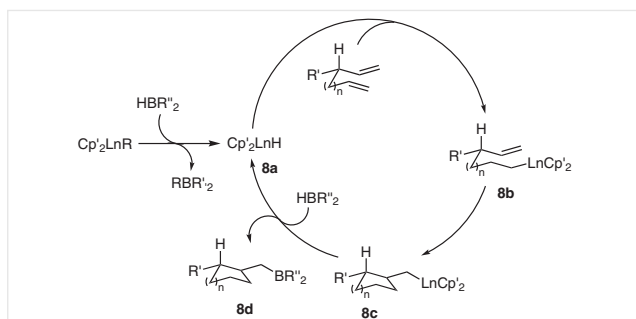


**Scheme 6** Hydroboration of hexa-1,5-diene by HBpin



**Scheme 7** Organolanthanide-catalyzed cyclization boration of 1,5- and 1,6-dienes

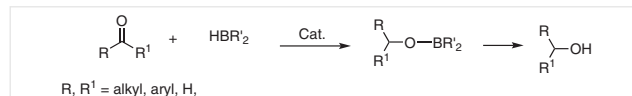
give metal hydrocarbyl compound **8b**. Subsequently, intramolecular cyclization between the metal species and another double bond followed by a  $\sigma$ -bond metathesis with another molecule of the organoborane gives the desired cyclic product **8d** and simultaneously regenerates the lanthanide hydride species.



**Scheme 8** Proposed mechanism for organolanthanide-catalyzed cyclization boration

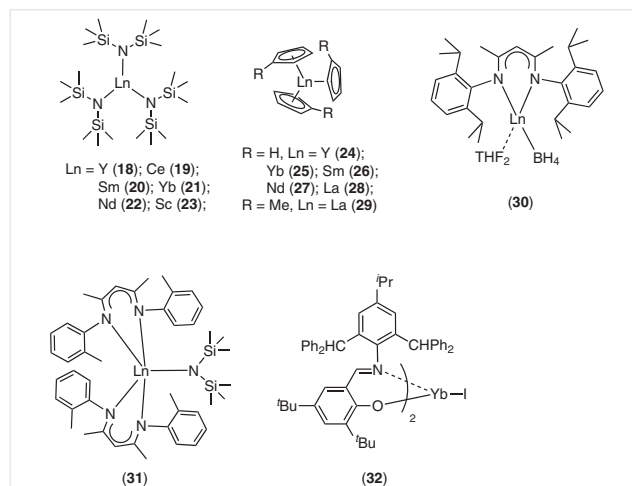
Koga and Kulkarni investigated  $\text{Cp}_2\text{SmH}$ -catalyzed ethylene hydroboration by ab initio MO methods.<sup>33</sup> In their calculations, ethylene coordinates to the samarium center to form a  $\pi$ -complex in the first step. Subsequent insertion of the ethylene molecule into the Sm–H bond through an energy barrier of 4.2 kcal/mol gives intermediate  $\text{Cp}_2\text{SmC}_2\text{H}_5$ , which could coordinate with a borane reagent  $\text{HB}(\text{OH})_2$  to yield a samarium metallacycle intermediate bridged with hydride and OH groups, respectively. Releasing the product  $\text{C}_2\text{H}_5\text{B}(\text{OH})_2$  is the final step, which also gives back the original active species, this step is also calculated as the rate-determining step.

### 3 Carbonyl Hydroboration



**Scheme 9** Schematic profile for the carbonyl hydroboration

Hydroboration of carbonyl compounds serves as an efficient strategy to access primary and secondary alcohols (Scheme 9). Comparing to reductions by active hydride reagents, such as  $\text{NaBH}_4$ ,  $\text{LiBH}_4$ , etc., carbonyl hydroboration generally displays good functionality tolerance, highly catalytic efficiency, outstanding selectivity, etc., and thus it has attracted great attention in the past few years.<sup>11k,25a,34</sup> The first examples of organo-*f*-element complex mediated carbonyl hydroboration was reported by the Marks group in 2017, in which the rapid, clean hydroboration of ketones and aldehydes with HBpin was achieved in the presence of the homoleptic lanthanide amide complexes **13** and **18–20** (Figure 3).<sup>35</sup> The reaction of benzophenone catalyzed by 0.01 mol% of complex **13** gave ~99% of the hydroboration product in less than 5 minutes; the TOF was measured to be 40,000  $\text{h}^{-1}$ .



**Figure 3** Organolanthanide complexes **18–32** for carbonyl hydroborations

Complexes **18–20** also revealed high efficiencies, but with relative smaller reactivities. Subsequent scope studies by using complex **13** demonstrated that the hydroboration of both electron-rich aliphatic ketones and less electron-rich aromatic ketones proceeded smoothly, but that the former required lower catalyst loadings (0.01 mol% vs 0.1 mol%). High selectivity and good functionality compatibility were also demonstrated from the ketone hydroboration reaction with various types of functional groups, such as halogens, nitro, alkenes, alkynes, etc., which successfully



survived during the reaction, and HBpin exclusively inserts into the carbonyl bond. Besides ketones, aldehydes can also be cleanly reduced.<sup>25a</sup>

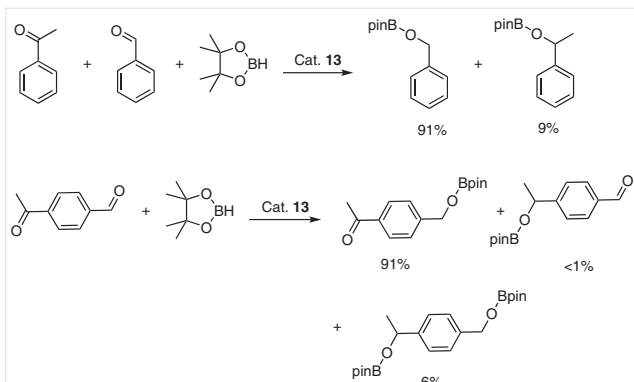
The rate laws for ketone and aldehyde hydroboration were respectively determined by using dicyclohexyl ketone and cyclohexanecarbaldehyde as substrates. For ketone hydroboration, first-order dependence on catalyst, ketone, and HBpin was revealed (Equation 1), with activation parameters of  $\Delta H^\ddagger = 17 \pm 1$  kcal/mol and  $\Delta S^\ddagger = -15 \pm 2$  e.u., respectively. For the aldehyde hydroboration, first-order dependence on precatalyst and zero-order dependence on aldehyde and HBpin was observed (Equation 2), with thermodynamic activation parameters of  $\Delta H^\ddagger = 12 \pm 2$  kcal/mol and  $\Delta S^\ddagger = -33 \pm 7$  e.u., respectively. The large enthalpy  $\Delta H^\ddagger$  in ketone hydroboration reflected unfavorable steric repulsions in the transition state. Therefore, when an equimolar mixture of acetophenone and benzaldehyde was reacted, a preference for aldehyde hydroboration was observed, with 91% conversion for benzaldehyde and 9% conversion for acetophenone. In a similar competition experiment, the reaction of 4-acetylbenzaldehyde with 1.0 equivalent HBpin was studied, and preferential hydroboration of the aldehyde (91%) was again observed (Scheme 10).

$$\frac{\partial p}{\partial t} = k [\mathbf{13}]^1 [\text{ketone}]^1 [\text{HBpin}]^1 \quad (1)$$

**Equation 1** Hydroboration of ketone by complex **13**

$$\frac{\partial p}{\partial t} = k [\mathbf{13}]^1 [\text{aldehyde}]^0 [\text{HBpin}]^0 \quad (2)$$

**Equation 2** Hydroboration of aldehyde by complex **13**



**Scheme 10** Competition studies between ketone and aldehyde hydroboration

Xue, Shen, and co-workers also employed complex **13** to promote ketone and aldehyde hydroborations, and substantially high catalytic efficiencies were revealed.<sup>36</sup>

In 2017–2018, Xue, Bao, Shen, and co-workers reported that homoleptic cyclopentadienyl lanthanide complexes **24–29** (Figure 3) served as excellent catalysts for the hydro-

roboration of carbonyl compounds with HBpin.<sup>37</sup> The reduction process can be carried out in various organic solvents, including toluene,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ , and even THF, DME, and 1,4-dioxane. This has great advantages compared to other organo-*f*-element complex mediated transformations as THF, DME, and 1,4-dioxane are generally considered as solvent-poisons to organo-*f*-element catalysts. Similar to Marks' report, complexes **24–29** also displayed good functionality tolerances, and they can selectively hydroborate the carbonyl bond while not reacting with other functional groups, such as halides, nitro group, etc. High chemoselectivity was also revealed from these systems, even at high conversions of the carbonyl group, where other unsaturated bonds, such as cyano, alkyne, alkene, remained intact throughout the reaction. Perhaps due to the less electrophilic and sterically more congested carbonyl center in ketones, they generally displayed sluggish reactivities compared to their aldehyde counterparts, this is consistent with other transition metal and main group metal complexes,<sup>12g,34c</sup> but opposite to the results obtained for lanthanide amide complexes.<sup>35</sup> Also for steric reasons, in competitive aldehyde/ketone hydroboration studies (similar to Scheme 10) mediated by complex **28**, aldehydes are preferentially reduced rather than ketones under identical conditions. During kinetic studies, it was found that the rates follow first-order dependence on aldehyde/ketone, HBpin, and complex **28**, respectively, giving the kinetic rate law shown in Equation 3.

$$\frac{\partial p}{\partial t} = k [\mathbf{28}]^1 [\text{ketone/aldehyde}]^1 [\text{HBpin}]^1 \quad (3)$$

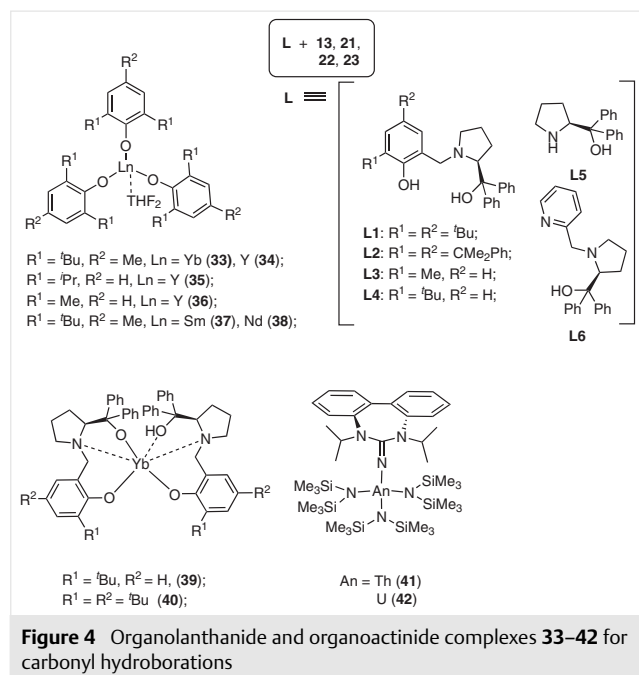
**Equation 3** Hydroboration of ketone/aldehyde promoted by complex **28**

Xue, Shen, and co-workers also utilized the  $\beta$ -diimide bivalent rare-earth borohydride complexes **30** and bis( $\beta$ -diimide) rare earth amide complexes **31** to catalyze the hydroboration between borane reagents and carbonyl compounds. The reactions rapidly, mildly, and efficiently gave the corresponding alcohol products.<sup>38</sup>

In 2018, Ma and co-workers, reported the hydroboration of aldehydes and ketones by the well-defined Schiff base heavy rare-earth ytterbium iodide complex **32**.<sup>39</sup> Similar to other light rare-earth complexes, this complex also displayed good functionality tolerances, and the presence of electron-withdrawing and -donating groups showed little influence on the hydroboration rate; the target pinacolboronate esters were obtained with high conversions in very short reaction times. Hydroboration of more sterically bulky ketone substrates, as expected, required higher catalyst loadings than those of aldehyde substrates, reflecting a sluggish reactivity therein. Under identical conditions, it was found that complex **32** exhibited higher activity in the hydroboration of aldehydes, such as  $\alpha,\beta$ -unsaturated

cinnamaldehyde, than the lanthanide amide complex **13** and cyclopentadienyl lanthanide complex **28**.

Lanthanide aryloxides **33–38** (Figure 4) were evaluated as catalysts by Xue, Bao, and co-workers in the hydroboration of carbonyl compounds with HBpin.<sup>40</sup> It was found that the complexes containing bulkier ligands have superior activities compared to their sterically less hindered counterparts. For instance, reducing the steric hindrance of *ortho*-substituents from *tert*-butyl (**34**) to isopropyl (**35**) and methyl (**36**) resulted in a reduction in alcohol conversions from 77% to 58%. Moreover, for lanthanides bearing the same ligands, the central Ln metals demonstrated that the order of catalytic reactivity follows Nd (**38**) > Sm (**37**) > Y (**34**) ~ Yb (**33**), with complex **38** as the optimal catalyst. In the presence of 0.05 mol% of complex **38**, most aromatic aldehydes were fully converted in 10–30 min, and functional groups, including heterocycles, halides, hydroxy, etc., showed a small influence on the reaction; the corresponding alcohols can be achieved with high catalytic efficiencies. Beside aldehydes, ketones can also be hydroborated smoothly by complex **38**, but with relatively lower reactivity, which is consistent with other lanthanide-mediated systems.

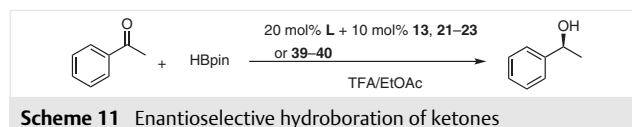


**Figure 4** Organolanthanide and organoactinide complexes **33–42** for carbonyl hydroborations

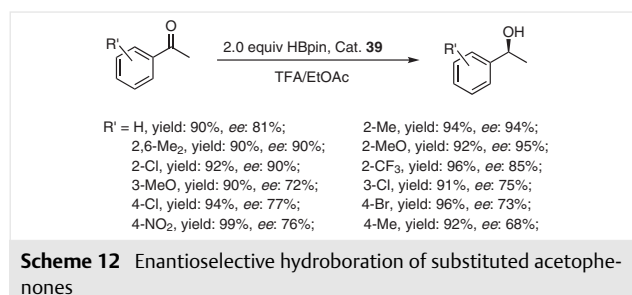
This superior reactivity of aldehydes over ketones was computationally evaluated, in which the energy barrier for the rate-determining step for ketones is ca. 5 kcal/mol higher than that of the aldehydes, thus preferable hydroboration of aldehydes was generally observed.

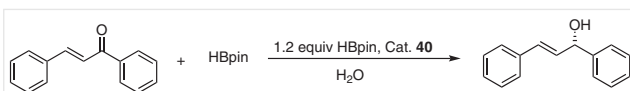
Stereoselective hydroboration/reduction of ketones employing efficient catalysts bearing chiral ligands has been rarely investigated.<sup>41a–d</sup> In 2018, Yao, Zhao, and co-workers

reported the only example of an enantioselective reduction of ketones catalyzed by rare-earth metal complexes with phenoxy modified chiral prolinols (Scheme 11, Figure 4).<sup>41e</sup> This reaction was catalyzed by the in situ formed complexes from 20% mol of the phenoxy-functionalized chiral prolinol ligand **L1** and 10 mol% of the lanthanide amide precursors **13** and **21–23**. The hydroboration reaction proceeded smoothly to afford the reduced alcohols in high yields. Additionally, it was found that lanthanide complexes with a central metal of moderate ionic radii, such as ytterbium amides **21**, resulted in much higher ee values (40%), than lanthanide counterparts with larger (28% ee for **13** and 31% ee for **22**) or smaller ionic radii (8% ee for **23**). This is perhaps due to the size of the ligand matching well with the appropriate ionic radii of the ytterbium metal, which plays a pivotal role in controlling the enantioselectivity of the active species. Varying ligand frameworks **L1–L6** (Figure 4), together with precursor **21** (Figure 3), demonstrated that the phenoxy ligand is essential for the enantioselectivity, and bulkier substituents, such as *tert*-butyl at the *ortho*-position, generally resulted in higher ee values. Well-defined ytterbium complex **39** was also evaluated as a catalyst, due to its structural similarity to the in situ formed active species, and better conversions (up to 96%) and ee value (up to 81%) were observed.



Substrate scope studies on various substituted acetophenones showed that enantioselective reductions can be performed smoothly with complex **39**. The presence of both electron-donating and -withdrawing groups gave the targeted alcohols in high yields (Scheme 12), but with varying ee values. In general, it was concluded that substrates bearing *ortho*-substituents gave good-to-excellent enantioselectivities, while *meta*- or *para*-substituted counterparts resulted in relative lower ee values. The enantioselective reduction of an  $\alpha,\beta$ -unsaturated ketone, chalcone, was also examined. In the presence of complex **40**, the corresponding alcohol was obtained with up to 99% conversion and

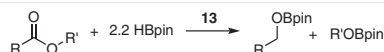




**Scheme 13** Enantioselective hydroboration of an  $\alpha,\beta$ -unsaturated ketone

83% ee; the double bond remained intact throughout the hydroboration (Scheme 13).

In 2019, Marks, Lohr, and co-workers reported an efficient, highly active, and selective homogeneous catalyst **13** for ester reduction with HBpin.<sup>42</sup> In the presence of 1 mol% of **13**, various types of esters were reduced in near quantitative yields at 25 °C or 60 °C, affording the target hydroborated alcohol products (Scheme 14). Steric impediments at the alkoxy position ( $R'$ ) significantly depress the reactivity, for instance, substrates with *tert*-butyl acetate required 16 hours to complete the reaction, whereas cyclohexyl or ethyl acetate required only 1 hour and 10 minutes, respectively. Comparatively, steric impediments at the acetyl position ( $R$ ) displayed little influence on the reactivity. Besides steric effects, a significant increase in turnover was observed for substrates with electron-withdrawing substituents at the  $R$  position. Additionally, the charge density on the alkoxy group also played a pivotal role in determining the reactivity; the presence of a phenyl group at the  $R'$  position reduced the rate dramatically. During the reduction, side reactions with nitro and alkenyl groups were not detected, demonstrating a high selectivity for the reaction. Competitive reactions between ester and oct-1-ene or oct-1-yne resulted exclusively in the reduction of the ester group.

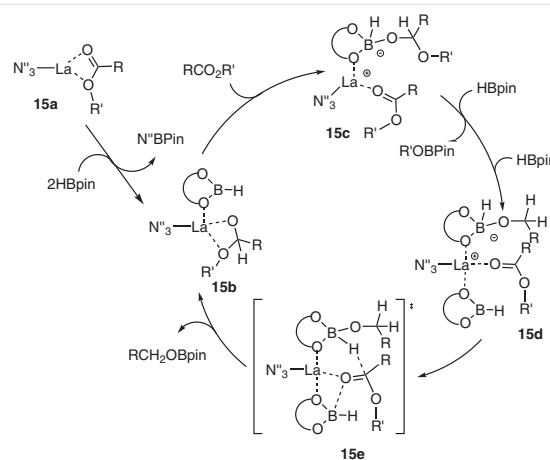


**Scheme 14** Ester hydroboration with HBpin promoted by complex **13**

Kinetic investigations for the ester hydroboration revealed first-order dependence on catalyst **13**, and zero-order dependence on both HBpin and the ester substrate, giving the rate law shown in Equation 4. Based on stoichiometric reactions and DFT calculations, a probable mechanism is proposed in Scheme 15. Activation of the ester coordinated complex **15a** with HBpin, followed by coordination of another molecule of HBpin, gives the hemiacetal active species **15b**. The HBpin molecule in this intermediate promotes La–O bond dissociation and B–O bond formation to generate intermediate **15c**, which is simultaneously stabilized by one molecule of ester. Intramolecular rearrangement yields product  $R'OBpin$ , followed by coordination of another molecule of HBpin to give intermediate **15d**. Final hydride transfer from the boron atom of the hydroborate–La complex to the coordinated ester **15e** regenerates the active species **15a**, and concurrently release the product of  $RCH_2Bpin$ .

$$\frac{\partial p}{\partial t} = k [\mathbf{13}]^1 [\text{ester}]^0 [\text{HBpin}]^0 \quad (4)$$

**Equation 4** Kinetic rate law in the hydroboration of esters by complex **13**



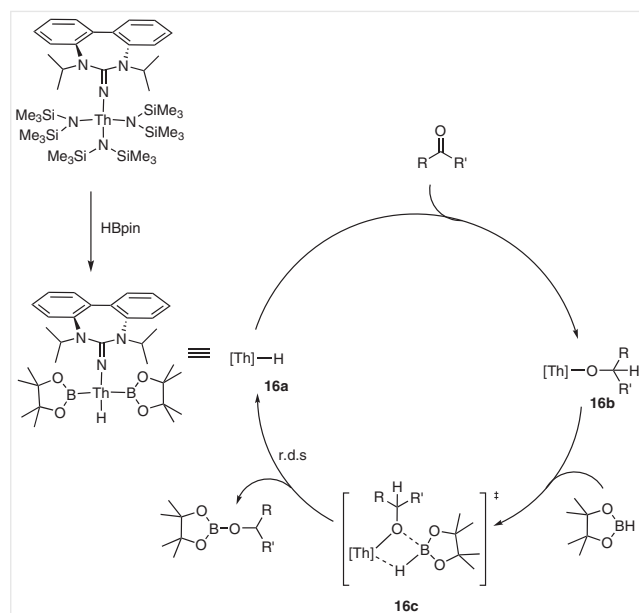
**Scheme 15** Proposed mechanism for ester hydroboration

Different from other metal complexes, transforming oxygen-containing substrates is a great challenge for organoactinides due to the high oxophilicity of the actinide center.<sup>1d–f,5</sup> By using strongly basic and highly nucleophilic imidazolin-2-iminato ligands, the Eisen group found that organoactinides can successfully transform oxygenated substrates, such as by the Tishchenko reaction,<sup>43</sup> ring-opening polymerization of cyclic ester,<sup>44</sup> insertions of alcohol into carbodiimides,<sup>6d,e,45</sup> etc. In 2018, the Eisen group reported an unprecedented chemoselective hydroboration of ketones and aldehydes catalyzed by the actinide complexes **41** and **42** (Figure 4).<sup>46</sup> This study not only demonstrated again the feasibility of transforming oxygen-containing substrates, but also investigated the possibility of regenerating an An–H bond from a thermodynamically stable An–O bond. In the presence of 0.1 mol% to 0.004 mol% of the complexes **41** and **42**, carbonyl compounds were hydroborated with HBpin in almost quantitative conversions in 15 minutes, and with TOFs as high as 100,000 h<sup>–1</sup>, which is highest value ever reported for a hydroboration process. Despite of the high oxophilicity of the metal center, complex **41** revealed good tolerance towards different types of functional groups, such as amine, imine, halides, nitro group, ester, etc., and afforded the corresponding alcoholic boronate esters in high yields. Furthermore, no hydroboration occurred on other unsaturated bonds, such as alkenes, alkynes, or the cyano group, even in the presence of excess HBpin, demonstrating the high chemoselectivity for this system. It is important to note that the present catalytic system displays a ‘living’ behavior, and in three consecutive



runs of adding substrates into the same reaction mixture, high catalytic reactivities were always successfully retained.

Based on stoichiometric reactions, a plausible mechanism was proposed (Scheme 16) in which the actinide monohydride intermediate **16a**, generated from the protonolysis of complex **41**, serves as the active species. This species further inserts into the carbonyl moiety to form the corresponding alkoxo complex **16b**. Subsequent  $\sigma$ -bond metathesis, with HBpin, gives the boronate ester product and regenerates simultaneously the active species **16a**. The kinetic rate law measured indicates a first-order dependence on catalysts, HBpin, and the carbonyl motif. Activation parameters were determined from the Eyring and Arrhenius plots, with values of 25.4 (0.8) e.u. for  $\Delta S^\ddagger$ , 13.7(0.7) kcal/mol for  $\Delta H^\ddagger$ , and 14.3(0.7) kcal/mol for  $E_a$ . Deuterium isotope studies using DBpin revealed that the reaction exhibited a KIE ( $k_H/k_D$ ) of 2.51 (0.07), indicating that the hydride transfer is the rate-determining step.

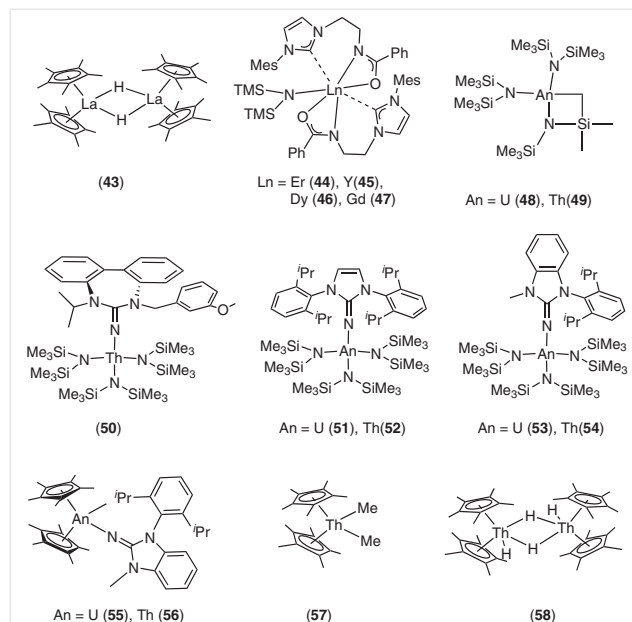


**Scheme 16** The proposed mechanism for organoactinide mediated hydroboration of carbonyl compounds

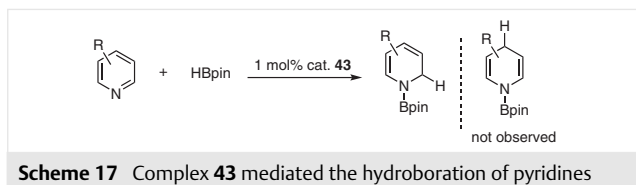
## 4 Imine and Nitrile Hydroboration

Reduction of imines and nitriles is a crucial methodology to access primary and secondary amines, which are extensively present in natural products, drugs, polymers, and other industrial and academic encounters. Compared to direct reduction by hydrogenation,<sup>47</sup> or alkaline metal hydrides,<sup>48</sup> the hydroboration generally displays a high efficiency, and a high selectivity under mild conditions, and

thus it has attracted much academic interest in over the past few years. To date, diverse Co,<sup>49</sup> Mg,<sup>11f,j</sup> Ru,<sup>50</sup> Mo,<sup>51</sup> Au,<sup>52</sup> etc., complexes have been extensively studied for the hydroboration transformation; organo-*f*-element catalysts, however, are relatively less utilized. The first report on the organolanthanide-mediated hydroboration of a C=N moiety appeared in 2014 by the Marks group, in which pyridines were regioselective 1,2-dearomatized by lanthanum hydride complex **43** to give 1,2-dihydropyridines (Figure 5).<sup>53</sup> Compared to previous dearomatization catalytic systems,<sup>11i,54</sup> the advantages of this research include the employment of earth-abundant, low toxic, low-cost lanthanide complexes that have high atom-efficiency and high 1,2-regioselectivity at low catalyst loading (1 mol%) under mild conditions (Scheme 17). Furthermore, good functional group compatibility was demonstrated for this system, despite the highly electrophilic nature of the lanthanide center. A wide range of pyridines possessing different types of functionalities, such as halides, methoxy, aryl groups, etc., underwent efficient hydroborations to give the target dearomatized products in moderate to high yields. Both electronic and steric factors were found to significantly influence the catalytic activities. The presence of electron-withdrawing groups led to increased hydroboration rates, and conversely, the presence of electron-donating groups resulted in lower TOFs. Besides pyridines, other benzofused *N*-heterocycles, including quinoline, isoquinoline, were hydroborated rapidly, affording the corresponding 1,2-dearomatized products in high yields.



**Figure 5** Organolanthanide and organoactinide complexes for imine and nitrile hydroborations



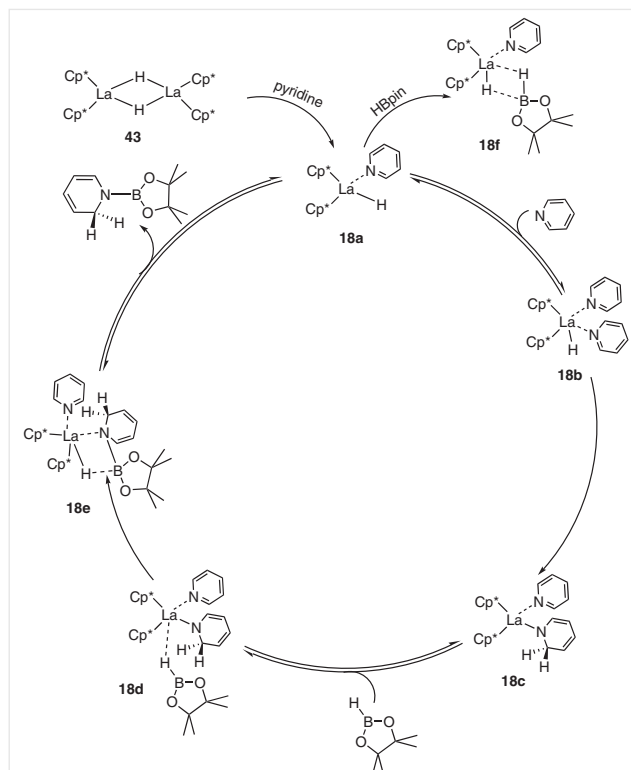
Kinetic studies revealed that the reaction rate was first order for the concentration of catalyst **43**, and inverse first order for HBpin. For pyridine concentration, however, the reaction rate law was first order when it was below 0.2 M, while zero-order at higher concentrations (Equation 5). The thermodynamic activation parameters, determined from the Eyring and Arrhenius plots, were  $\Delta H^\ddagger = 15.7(0.5)$  kcal/mol,  $\Delta S^\ddagger = -27.2(0.3)$  cal/mol, and  $E_a = 14.3(0.7)$  kcal/mol.

$$\frac{\partial p}{\partial t} = k [\mathbf{43}]^1 [\text{HBpin}]^{-1} [\text{Py}]^x \quad x = 0, 1 \quad (5)$$

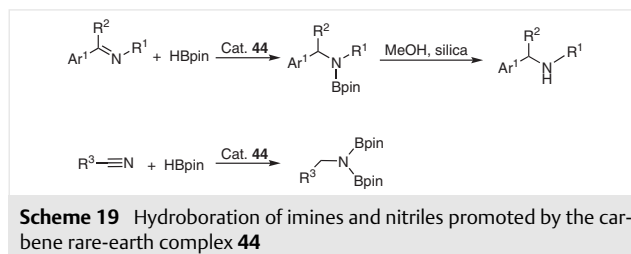
**Equation 5** The rate law for the hydroboration of pyridine mediated by complex **43**

A plausible mechanism for this hydroboration process is proposed (Scheme 18) based on the stoichiometric reaction and DFT calculations. In the presence of pyridine, the dimeric complex **43** is firstly cleaved into the monomeric adduct  $\text{Cp}^*_2\text{LaH}(\text{Py})$  (**18a**), which then could be coordinated by a second molecule of pyridine to form the bispyridine adduct  $\text{Cp}^*_2\text{LaH}(\text{Py})_2$  (**18b**). This bispyridine adduct undergoes La–H 1,2-insertion across the aromatic C=N moiety to afford a  $\text{Cp}^*_2\text{La}(\text{NC}_5\text{H}_6)(\text{Py})$  complex **18c**, which is further identified as one of the two rate-determining steps by DFT calculations. In the presence of a molecule of coordinated HBpin, La–N/H–B  $\sigma$ -bond metathesis quickly occurs, and releases the final desired N-borylated 1,2-dihydropyridine, with simultaneous regeneration of **18a**. During the catalytic process, a rapid equilibrium between **18a** and **18f** was also established, which represents a deactivation pathway during the catalytic process.

In 2018, Wang and co-workers reported the hydroboration of a large number of imines and nitriles using amide-functionalized *N*-heterocyclic carbene rare earth complexes **44–47** as catalysts.<sup>55</sup> They found that these complexes displayed high catalytic activity for the hydroboration of *N*-benzylideneaniline affording the desired hydroborated product in high yields. Under identical conditions, complexes **44–47** also demonstrated much better reactivities than other amido metal complexes, such as  $\text{NaN}(\text{SiMe}_3)_2$ ,  $\text{KN}(\text{SiMe}_3)_2$ ,  $\text{Gd}[\text{N}(\text{SiMe}_3)_2]_3$ ,  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (RE = Er, Y, Dy), indicating the important role of the carbene moiety in enhancing the catalytic activity. Studies of the substrate scope by varying  $\text{R}^1$  and  $\text{R}^2$  (Scheme 19, top) revealed that substituents with different electronic properties, such as alkyl, halides, methoxy, naphthyl, and hydroxy, showed little influence on the yields of the desired prod-

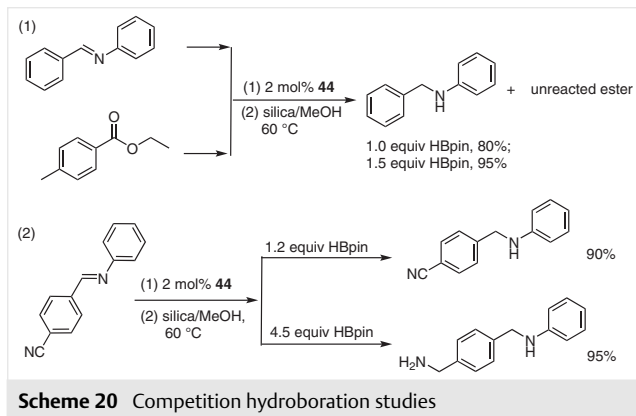


ucts. The reaction performed with the strong electron-withdrawing nitro group was an exception, in which a relatively poor yield resulted due to the coordination of the nitrogen to the rare earth metal. Subsequent substrate expansion to nitrile compounds revealed that, in the presence of 3 equivalents of HBpin and 2 mol% of catalyst, aromatic and aliphatic nitriles can be double hydroborated, regardless of the electronic and steric effects, to afford the dihydroborated products in excellent yields (89–99%) (Scheme 19, bottom).

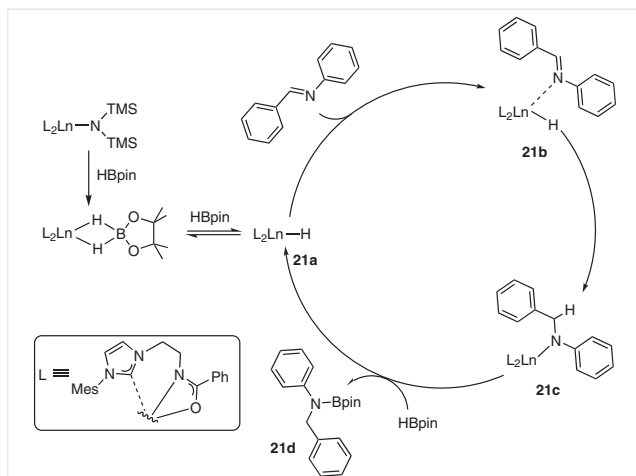


A series of competition reactions among different C=O, C=N, C≡N, CO<sub>2</sub>Et, and C=C groups were also carried out. The reactivity was found to follow the order of C=O >> C=N > C≡N > CO<sub>2</sub>Et > C=C. Hence, when a mixture of ethyl 4-methylbenzoate and *N*-benzylideneaniline was hydroborated, the exclusive hydroboration of the imine was observed

[Scheme 20, (1)]. For a substrate bearing both the cyano and imine groups, selective hydroboration on the imine was observed when 1.2 equivalents of HBpin were utilized, however, increasing the amount of HBpin to 4.5 equivalents led to a complete reduction of both imine and cyano groups [Scheme 20, (2)].

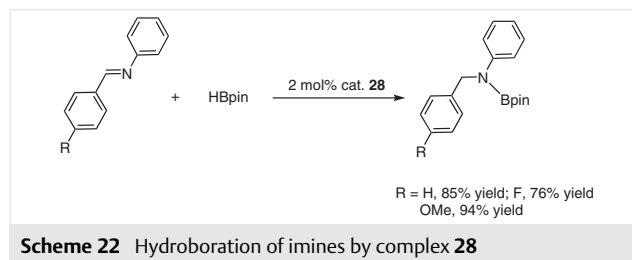


A plausible mechanism for the hydroboration of imines is presented as Scheme 21. In the presence of HBpin, the rare-earth metal hydride species **21a** is firstly generated, which subsequently inserts into a coordinated C=N imine bond to give the rare-earth amido intermediate **21c**. This intermediate reacts with another molecule of HBpin to release the desired hydroborated product **21d** and regenerate the active species **21a**.



Xue, Bao, and co-workers also reported that complex **28** (Figure 3) was an effective catalyst for the hydroboration of imines in addition to carbonyl substrates.<sup>37b</sup> In the presence of 1 equivalent of HBpin and 2 mol% of complex **28** at 60 °C, aromatic imine derivatives containing an electron-with-

drawing group (4-F) or an electron-donating group (4-MeO) delivered medium to good yields of the target products (Scheme 22).



Motivated by recent reports of organolanthanide-catalyzed hydroboration of C=N and C≡N moieties, the Eisen group developed a series of organoactinide complexes to perform similar transformations. Benzonitrile underwent double hydroboration catalyzed by the thorium metallacycle complex **49** (0.1–1 mol%) in a short reaction time to afford the dihydroborated amine in high yields.<sup>56</sup> This reaction was later expanded to other nitrile derivatives, and it was found that electron-rich aromatic nitriles bearing electron-donating groups such as 4-Me, 4-MeO, etc., displayed higher reactivities than electron-withdrawing counterparts for which longer reaction times or larger catalyst loadings were required in order to completely transform the nitrile reagents. Polyaromatic nitrile compounds, such as 1-naphthonitrile, showed lower reactivity compared to benzonitrile. However, heteroatom-containing aromatic nitriles, such as furanacetonitrile, thiopheneacetonitrile, pyridine-4-acetonitrile, underwent the double hydroboration efficiently affording the corresponding compounds almost quantitatively. Moreover, different from known catalysts, for less reactive for aliphatic nitriles, complex **49** showed remarkable turnover frequencies for aliphatic nitrile compounds, which are comparable to aromatic counterparts, demonstrating the unique advantage of the organoactinide complexes.

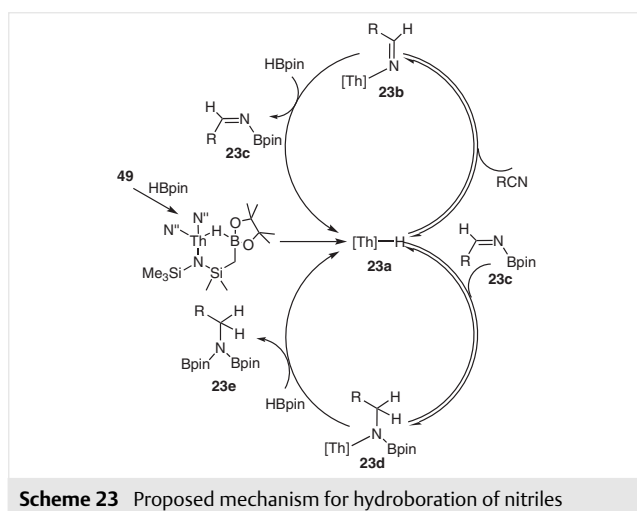
Kinetic measurements for the double hydroboration of benzonitrile revealed first-order dependence on the catalyst **49**, second-order dependence on HBpin, and zero-order dependence on benzonitrile, giving an equation as shown in Equation 6. Activation parameters were determined from the Eyring and Arrhenius plots with  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ , and  $E_a$  values of  $-47.25(1.23)$  e.u.,  $6.99(0.44)$  kcal/mol, and  $7.66(0.44)$  kcal/mol, respectively.

$$\frac{\partial p}{\partial t} = k [\mathbf{49}]^1 [\text{HBpin}]^2 [\text{PhCN}]^0 \quad (6)$$

**Equation 6** Kinetic rate law for hydroboration benzonitrile promoted by complex **49**

A plausible mechanism for the double nitrile hydroboration was proposed (Scheme 23). The activation of the catalytic cycle is firstly achieved by the protonolysis of complex

**49** to generate the thorium hydride species **23a**, which then quickly inserts into the C≡N bond, allowing the formation of intermediate **23b**. In the presence of HBpin, **23b** is able to undergo  $\sigma$ -bond metathesis to release the monohydroborated imine product **23c**, which quickly participates in the second catalytic cycle by coordinating back to active species **23a**. The Th–H moiety in **23a** quickly inserts into the C=N bond of **23c**, giving the intermediate **23d** bearing the dihydroborated amido substituent. In the presence of another molecule of HBpin, **23d** undergoes Th–N/HBpin  $\sigma$ -bond metathesis to give the final double hydroborated amine product **23e**, and concurrently regenerates the active species **23a**. Deuterium isotope analysis suggested that the final hydroboration step is the turnover-limiting step for the catalytic process.



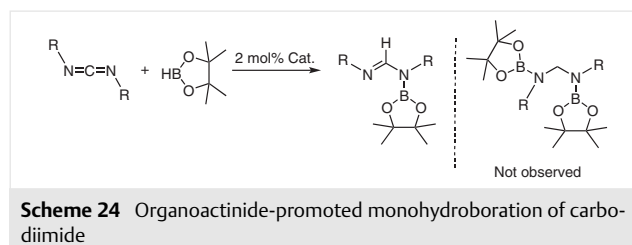
**Scheme 23** Proposed mechanism for hydroboration of nitriles

In addition to nitriles, complex **49** was also utilized in the hydroboration of imines.<sup>56</sup> Whereas the thorium complex **50** (Figure 5), coordinated by the seven-membered *N*-heterocyclic iminato ligand, showed much better catalytic efficiency. Moreover, complex **50** displayed large substrate scope capabilities, a large number of aldimines, including ketimines, were hydroborated to afford the corresponding products in almost quantitative yields. Aldimines comprising electron-donating functionalities increased the reactivities substantially, in comparison to the electron-withdrawing counterparts. Kinetic studies on the PhC=NPh/HBpin/**50** system revealed that the kinetic rate law follows has a first-order dependence on catalyst **50** and HBpin, and zero-order dependence on imine, giving rise to Equation 7.

$$\frac{\partial p}{\partial t} = k [\mathbf{50}]^1 [\text{HBpin}]^1 [\text{PhCNPh}]^0 \quad (7)$$

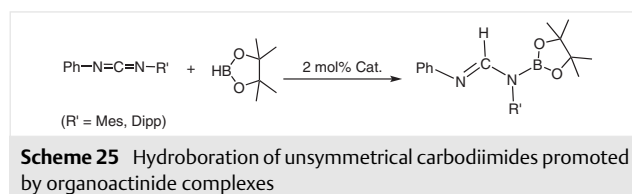
**Equation 7** Kinetic rate law for the hydroboration of imines mediated by complex **50**

The selective monohydroboration of carbodiimides is of great interest for scientists because the produced amidinates play a pivotal role in coordination chemistry. In 2018, the Eisen group reported a highly efficient and highly monoselective organoactinide-catalyzed hydroboration of carbodiimides using complexes **48** and **49** and **51–56** (Figure 5).<sup>57</sup> Different from the previously reported magnesium systems,<sup>11e,g</sup> the organoactinide complexes required lower catalyst loadings and shorter reaction times and exhibited, unprecedentedly, a monoselective reactivity (Scheme 24). Compared to the actinide amido complexes **48** and **49** and **51–54**, the actinide methyl counterparts displayed superior reactivities, affording the corresponding hydroborated products with higher yields under identical reaction conditions. Subsequently, the substrate scope revealed that steric properties played a significant role in determining the catalytic efficiency. For symmetrical carbodiimides bearing smaller groups, such as isopropyl, cyclohexyl, phenyl, etc., quantitative conversion can be achieved in shorter reaction times, while sterically congested counterparts require much longer reaction times to obtain a high conversion. Electronic properties showed a very small influence on the catalytic activities, affording the product in high yields.



**Scheme 24** Organoactinide-promoted monohydroboration of carbodiimide

An interesting phenomenon was observed when using unsymmetrical carbodiimide substrates. For the hydroboration of *N*-mesityl-*N'*-phenylcarbodiimide (MesNCNPh) and *N*-(2,6-diisopropylphenyl)-*N'*-phenylcarbodiimide (DippNCNPh), the Bpin group is selectively attached to the steric bulky side of the carbodiimide, rather than the steric opening side, affording *N*-{Bpin}-*N*-diisopropylphenyl-*N'*-phenylformamidinate and *N*-{Bpin}-*N*-mesityl-*N'*-phenylformamidinate as the sole reaction products (Scheme 25).



**Scheme 25** Hydroboration of unsymmetrical carbodiimides promoted by organoactinide complexes

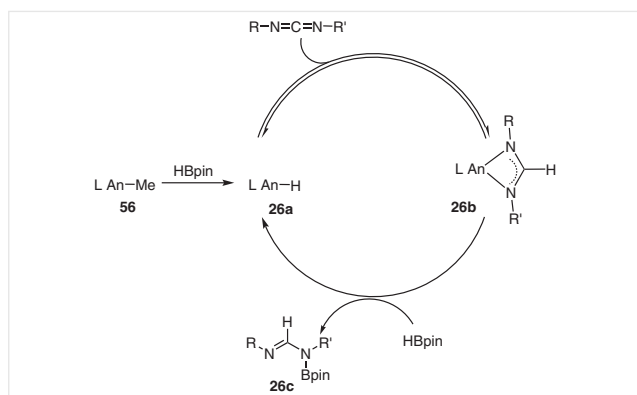
The thermodynamic activation parameters, determined from Eyring and Arrhenius plots, were  $E_a = 16.6(9)$  kcal/mol,  $\Delta H^\ddagger = 16.0(3)$  kcal/mol, and  $\Delta S^\ddagger = -27.7(6)$  e.u., respectively. Kinetic studies on the <sup>i</sup>PrNCN<sup>i</sup>Pr/HBpin/**56** system revealed

a first-order dependence on HBpin,  $i\text{PrNCN}i\text{Pr}$ , and **56**, respectively, giving rise to the kinetic rate law as presented in Equation 8.

$$\frac{\partial p}{\partial t} = k [\mathbf{56}]^1 [\text{HBpin}]^1 [i\text{PrNCN}i\text{Pr}]^1 \quad (8)$$

**Equation 8** The rate law for the hydroboration of carbodiimide catalyzed by complex **56**

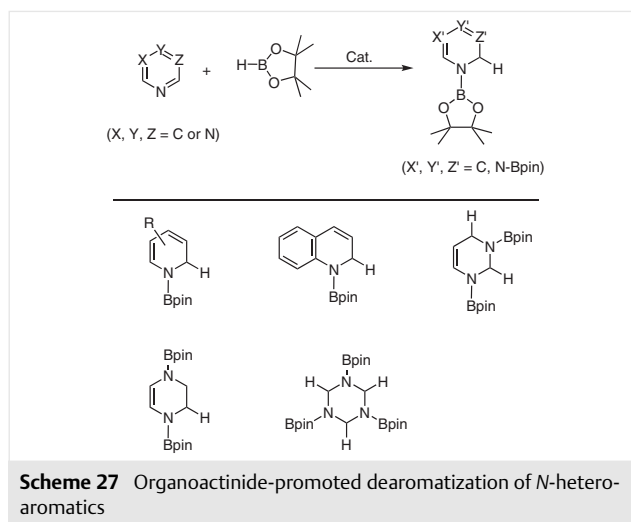
A plausible mechanism is proposed, based on stoichiometric reactions (Scheme 26). Firstly, a rapid  $\sigma$ -bond metathesis between the actinide methyl complex and HBpin occurs to yield the catalytic active species **26a**, which then inserts into the C=N bond of the carbodiimide substrate allowing the formation of actinide amidinate intermediate **26b**. In the presence of another molecule of HBpin, the monohydroborated carbodiimide **26c** is released as the final product with the concomitant regeneration of the active species **26a**.



**Scheme 26** Proposed mechanism for hydroboration of carbodiimides

Also in 2018, the Eisen group reported another example of a catalytic dearomatization/hydroboration of *N*-heteroaromatics utilizing the thorium complexes **57** and **58**.<sup>58</sup> In this research, complexes **57** and **58** displayed high catalytic activity in the hydroboration of pyridines, affording the 1-boryl-1,2-dihydropyridine product in high yields. Moreover, no 1,4-hydroborated product was detected during the reaction process, demonstrating a high 1,2-selective fashion (Scheme 27). Subsequent substrate studies revealed a large scope capability, and pyridines with different types of *meta*- and *para*-substituted groups, including alkyl, aryl, halides, nitro, methoxy, etc., were hydroborated by HBpin selectively affording the corresponding products in moderate to high yields.

Furthermore, other *N*-heteroaromatic compounds, such as quinoline, pyrazine, pyrimidine, triazine, etc., were also feasible for the hydroboration process, affording the mono-, di-, and trihydroborated products in high yields. It is important to note that the remaining double bond in the hydro-



**Scheme 27** Organoactinide-promoted dearomatization of *N*-heteroaromatics

borated pyridine product remained intact during the reaction, indicating a highly chemoselective fashion of the precatalysts.

Kinetic investigations of the pyridine/HBpin/**58** catalytic system revealed a first-order dependence on the concentration of pyridine, HBpin, and complex **58**, respectively, giving rise to the kinetic rate as shown in Equation 9. The thermodynamic activation parameters, determined from the Eyring and Arrhenius plots, are  $E_a = 20.3(1)$  kcal/mol,  $\Delta H^\ddagger = 19.6(5)$  kcal/mol, and  $\Delta S^\ddagger = -23.5(1)$  e.u., respectively.

$$\frac{\partial p}{\partial t} = k [\mathbf{58}]^1 [\text{HBpin}]^1 [\text{Py}]^1 \quad (9)$$

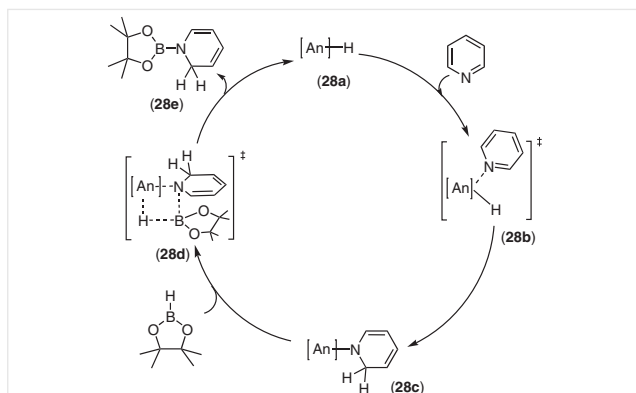
**Equation 9** The rate law for the hydroboration of pyridine catalyzed by complex **58**

A plausible catalytic mechanism was proposed (Scheme 28). The activation of the cycle is firstly achieved by the cleavage of the dimeric complex **58** (Figure 5) in the presence of pyridine to afford the monomeric complex **28a**. Subsequent insertion of the Th-H into the C=N moiety of pyridine gives the thorium amido intermediate **28c**. In the presence of HBpin, a subsequent Th-N/H-B  $\sigma$ -bond metathesis via the transition state **28d** affords the final hydroborated product **28e** and concurrently regenerates the active species **28a** to complete the cycle.

## 5 Conclusions and Outlook

In summary, we have extensively reviewed recent advances in organo-*f*-element complex mediated the hydroborations of alkenes, carbonyls, imines, and nitriles. Despite the highly oxophilic nature of the lanthanide and actinide metal centers, the complexes displayed high catalytic efficiencies and high selectivities throughout the transformations, even when using oxygen-containing borane reagents.





**Scheme 28** Plausible mechanism for pyridine hydroborations mediated by complex **58**

Noteworthy to point out that in the process of the hydroboration of carbonyl compounds, regeneration of  $\text{Ln-H}$  or  $\text{An-H}$  active species from  $\text{Ln-O}$  or  $\text{An-O}$  bonds is achieved, refreshing our traditional understanding of the expected sluggish  $\text{Ln-O}$  or  $\text{An-O}$  bonds. Another reaction that deserves attention is the dearomatization of  $N$ -heteroaromatics compounds by organo- $f$ -element complexes via hydroboration. Dearomatized  $N$ -heteroaromatics, such as 1,2-dihydropyridine, play a significant role in the pharmaceutical fields, and until now, only few catalytic systems were available to disrupt the aromaticity of  $N$ -heteroaromatics. Organo- $f$ -complexes displayed their unique advantage in this process when considering their high 1,2-regioselectivity, high catalytic turnovers, and more importantly, high earth abundance.

Despite the advances presented in this review, a large number of challenging and important reactions are still untapped. For example, the development and utilization of C1 sources ( $\text{CO}_2$  and  $\text{CO}$ ), which is a green and sustainable strategy to convert these gases into value-added C1 compounds, such as methanol, formic acid, etc. Many stoichiometric reactions between organo- $f$ -complexes with  $\text{CO}_2$  or  $\text{CO}$  have been reported,<sup>59</sup> and some transition metals catalyze the hydroboration of  $\text{CO}_2$ .<sup>60</sup> However, no reports on organo- $f$ -complexes mediating the hydroboration of  $\text{CO}_2$  or  $\text{CO}$  in a catalytic way have been disclosed. We need to ask, how far we can advance in transforming oxygen-containing substrates using organo- $f$ -complexes? Despite recent advances in transforming oxygen-containing substrates, such as alcohol,<sup>6c,d,f</sup> aldehyde,<sup>43a</sup> ester,<sup>42,44</sup> etc., how about more challenging substrates? Such as water? For example, catalytically making  $\text{H}_2$  from  $\text{H}_2\text{O}$ ; some uranium complexes have been reported to be feasible.<sup>61</sup> In general, organo- $f$ -element complex mediated hydroboration is still in its early stage; expansion into other substrates and deeper understanding of the catalytic mechanism of this type reaction is still required.

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