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Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide

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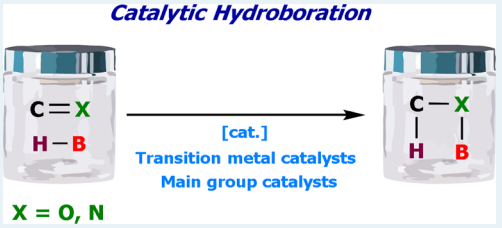
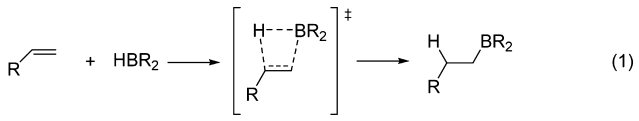
ABSTRACT: Organoborane compounds present a class of versatile synthetic intermediate for myriad organic transformations. The direct addition of a B−H bond across unsaturated bond—namely, hydroboration—is a powerful tool for the preparation of organoborane derivatives. This review outlines recent advances in catalytic hydroboration of unsaturated organic compounds, specifically those involving C-X (X = N, O) bonds. We will discuss the chemical behavior of both transition metal catalysts and main group catalysts in hydroboration. Emphasis will also be placed on the reaction mechanism of these catalytic reactions. Furthermore, recent achievements in catalytic hydroboration of carbon dioxide CO_2 will be highlighted.



KEYWORDS: *hydroboration, boranes, transition metal catalysis, main group catalysis, CO_2 reduction*

1. INTRODUCTION

Organoboranes are significant synthetic intermediates in a variety of organic transformations. In 1956, H. C. Brown et al. observed the direct addition of a boron−hydrogen bond across C═C—namely, hydroboration—in the reaction of alkenes with sodium borohydride-aluminum chloride.[1] Around the same period, R. Köster et al. also reported the hydroboration of alkenes using alkylboranes.[2] These discoveries marked a significant milestone in hydroboration and paved the way for the development of many important organic transformations.[3−5] Hydroboration occurs readily when an alkene reacts with the simplest boron reagent, BH_3, to yield an anti-Markovnikov product (eq 1). Regioselectivity of the



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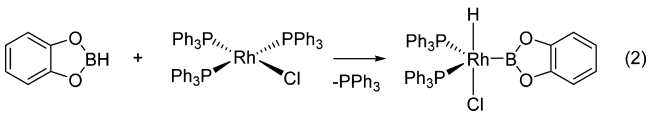

(2)

reaction can be rationalized by three main factors: first, the addition of B−H bond occurs in a cis fashion; second, the boryl BH_2 moiety prefers the least sterically hindered carbon; and last, the partial charges suggest that the hydridic H in B−H favors interaction with a more positively charged carbon in the transition state.[6−9] Substituents on the carbon could stabilize the partial positive charge on the carbon, and therefore, hydride addition onto a more substituted carbon is preferred, although this transition state theory still remains controversial.[10,11]

Other borane reagents, such as pinacolborane (HBpin) or catecholborane (HBcat), can be used, but they are active only at elevated temperatures, possibly because of the significant decrease in Lewis acidity. On the other hand, it has been reported that hydroboration of alkenes and alkynes using the strong electrophilic Piers' borane $HB(C_6F_5)_2$ could occur even at room temperature.[12] In 1975, Kono and Ito et al. observed that the $Rh(PPh_3)_3Cl$ complex, also termed Wilkinson's catalyst, underwent oxidative addition with HBcat (eq 2).[13] A breakthrough came in 1985 when Männig and Nöth et al. demonstrated the first example of metal-catalyzed hydroboration of alkenes and alkynes using the Wilkinson's catalyst.[14] Later, Westcott et al. isolated and characterized the oxidative addition product of $HRhCl(P^iPr_3)_2(Bcat)$.[15]

Following pioneering work, numerous research groups have developed hydroboration of carbon−carbon unsaturated bonds catalyzed by various transition metals.[16−19] Although the reaction mechanism of transition metal-catalyzed hydroboration of unsaturated C−C bonds has been extensively investigated with the help of labeling experiments and theoretical calculations, there is no common consensus on its mechanistic steps or transition states. Nonetheless, the general mechanism can be summarized as follows (Scheme 1): an initial oxidative addition of the B−H bond at the metal center is followed by the π-coordination of the unsaturated C−C bond to the metal center. Subsequent migration of hydride would occur to either the terminal or the substituted carbon atom. Last, reductive elimination from the metal center would yield the hydroborated products and regenerate the metal catalyst.

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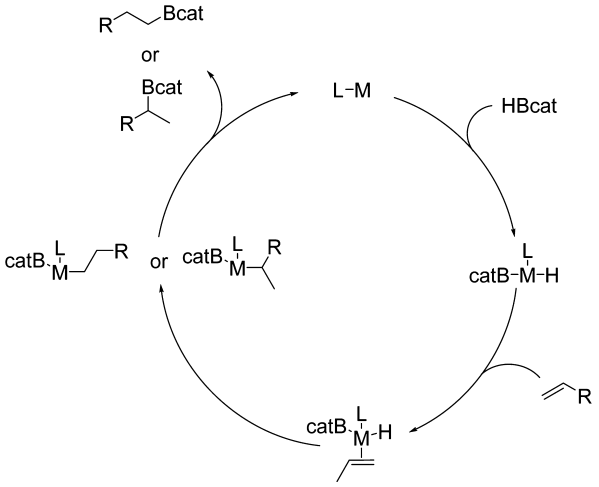
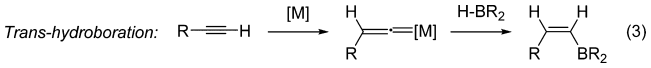
Scheme 1. General Mechanism for Transition Metal-Catalyzed Hydroboration of Alkenes



The chemoselectivity and regioselectivity as well as enantioselectivity of the catalytic reaction vary, depending on the metal center, ligands, and the substrates. For instance, seminal work by Miyaura et al. demonstrated that the unusual trans addition for the hydroboration of alkynes could be obtained using Rh or Ir catalysts in the presence of NEt_3 as the base.[20] More recently, Leitner et al. and Fürstner et al. also developed Ru-based catalytic system for the synthesis of (*Z*)-alkenylboron compounds.[21,22] In these trans-hydroboration reactions, the mechanism usually involves the formation of metal vinylidene complex as the key intermediate (eq 3). In



comparison with the well-established hydroboration of unsaturated C−C bonds, fewer studies on the catalytic hydroboration of other unsaturated bonds, such as C═O or C═N, have been reported thus far. Over the past decade, the number of reports on both transition metal- and nontransition metal-catalyzed hydroboration of carbonyl compounds as well as imine derivatives has increased gradually.

In this review, we will outline the recent developments of transition metal-catalyzed hydroboration toward unsaturated bonds, such as C═O and C═N. The use of various transition metals in catalytic hydroboration reactions and the reaction mechanisms are described. In view of the increasing prominence of catalytic hydroboration using main group compounds, we will also discuss in depth the reaction mechanism of main group compound-catalyzed hydroboration reactions. Moreover, recent progress on hydroboration of carbon dioxide will be summarized in detail.

2. TRANSITION METAL CATALYZED-HYDROBORATION OF CARBONYL COMPOUNDS

Reduction of carbonyl compounds is one of the useful synthetic routes to alcohols that are industrially important compounds produced in bulk.[23,24] Archetypal reduction process of carbonyl compounds involves the use of metal hydrides or transition metal-catalyzed hydrogenation.[25−29] Meanwhile, catalytic hydrosilylation and hydroboration of carbonyl compounds have been gaining interest because of the mild reaction conditions, which avoid the use of flammable, highly pressurized H_2 gas. Conventional methods of hydroboration involve the stoichiometric addition of BH_3 to carbonyl compounds to form borates, which can be easily hydrolyzed to alcohol.

2.1. Ti Complex-Catalyzed Hydroboration of C═O.

Titanium alkoxides present the initial examples of transition metal complexes utilized in the catalytic hydroboration reaction of carbonyl compounds. In 1994, DiMare and co-workers reported that the use of a stoichiometric amount of $TiCl_4$ accelerated the reduction of ketones.[30] Subsequently, DiMare et al. discovered that 5 mol % of $Ti(OiPr)_4$ effectively promoted the reduction of acetophenone with HBcat or BH_3.[31] The reduction occurred readily (30 min with HBcat, less than 1 min with BH_3) at 20 °C to give the corresponding alcohol in excellent yields (93−95% isolated yields). They also demonstrated that the asymmetric reduction of acetophenone was possible with Ti-TADDOL complex **1a**, although a poor ee of 24% was observed (Figure 1) (Scheme 2a). The mechanism for

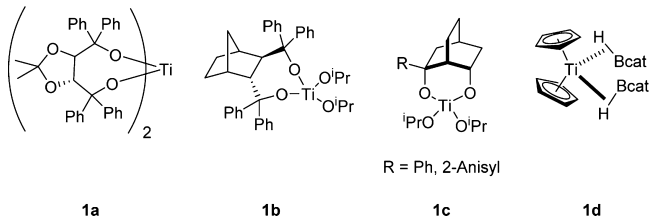
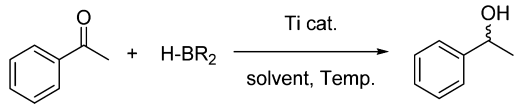


Figure 1. Ti-complexes used in catalytic hydroboration of ketones.

Scheme 2. Conditions Used for Various Ti-Catalyzed Hydroboration of Acetophenone, Reported by (a) DiMare, (b) Wandrey, (c) Frejd and, (d) Muhoro



[a]DiMare: $Ti(OiPr)_4$ (10 mol %) or **1a** (5 mol %), BH_3 or HBcat (**1** equiv), CH_2CI_2, 20 °C. [b]Wandrey: **1b** (10 mol %), HBcat (1.1 equiv), hexane, −30 °C (82% ee, *S* configuration). [c]Frejd: **1c** (R = 2-anisyl) (10 mol %), HBcat (1.5 equiv), hexane, −20 °C (96% ee, *R* configuration). [d]Muhoro: **1d** (5 mol %), HBpin (1 equiv), C_6D_6, r.t.

the catalytic cycle has not been clarified, but DiMare et al. highlighted the rapid formation of a deeply colored alkoxyborohydride $HB(OiPr)_2$ upon addition of $Ti(OiPr)_4$ to HBcat or BH_3.

Wandrey and Frejd's groups independently revealed that titanium-alkoxide complexes (**1b,c**) generated in situ from the reaction of $Ti(O^iPr)_4$ with TADDOL-analogous ligands, were efficient in reduction of acetophenone to give 1-phenylethanol (Scheme 2b,c).[32,33] With HBcat (1.1 equiv) in the presence of **1b** (10 mol %), the reaction was completed within 1 h (100% conversion and 82% ee). Changing the reductant to the BH_3·THF complex resulted in a dramatic decrease in ee values to 18%. Similarly, **1c** (R = 2-anisyl, 10 mol %) and HBcat (2 equiv) were able to reduce acetophenone within 7.5 h (47% yield, 89% ee). For both cases, however, the structural characterization of these Ti-alkoxide complexes was not accomplished, and thus, the actual active catalysts in the systems were unclear.

In 2001, Frejd et al. reported that the order of addition of the reagents as well as the dryness of the solvent were important to reproduce the efficient hydroboration reaction. Initially, both

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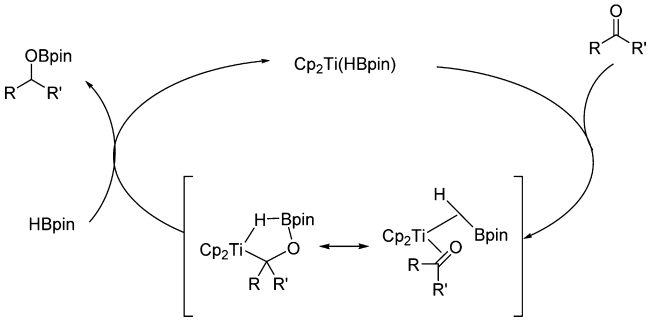
$Ti(O^iPr)_4$ and ligand were mixed and stirred in ^{t}BuOMe that was dried using molecular sieves. Ketone was then added to the mixture, followed by the addition of HBcat at −20 °C. They could increase the ee of the reduction product up to 96% using the same catalyst bearing the BODOL ligand **1c** (R = 2-anisyl).[34] Various ketone substrates were subjected to a similar sequence of addition and gave the corresponding secondary alcohols in good yields (50−97%). Meanwhile, no catalytic activity was observed for bulky isobutyrophenone substrate, probably due to steric reasons. Significantly, disproportionation of Ti-catecholates formed by the reaction of $Ti(OiPr)_4$ with HBcat could generate BH_3, which seemed not to be the actual reductant in this reaction. Attempts to elucidate the structure of the precatalyst were unsuccessful, but NMR analysis suggested that the precatalyst might contains two ligands coordinating to the Ti center in a dimeric form.

Recently, Muhoro et al. developed another Ti complex, **1d**, for the hydroboration of ketones and aldehydes (Scheme 2d).[35] The catalytic reaction with HBpin proceeded readily in the presence of 5 mol % of **1d**. Various substrates were screened at room temperature, which afforded the alkoxypinacolboronate esters in good yields (69−91%). More importantly, efforts were made by the authors to elucidate the mechanism in this reaction. First, a Hammett plot for the hydroboration of various arylketones suggested that the rate of reaction for electron poor ketones was much faster than for electron rich ketones. On the other hand, the yields of benzophenone (90%) and benzaldehyde (86%) were almost similar after 2.5 h at room temperature. Therefore, the authors mentioned that the electronic properties of the substrates were more important than the steric factors. A plausible mechanism of the reaction was proposed by the authors (Scheme 3). In advance of the

Scheme 3. Proposed Mechanism for $Cp_2Ti(HBcat)_2$-Catalyzed Hydroboration Reaction



catalysis, the dissociation of HBcat and coordination of HBpin is postulated to form the catalytically active species Cp_2Ti-(HBpin). The first step of the catalytic cycle consists of the coordination of ketone to form an η^2-C=O π coordinated complex with a Ti(II) center. Interestingly, computational studies implied that the structure of the reaction intermediate features a resonance hybrid between the Ti(II) η^2-C=O complex and the Ti(IV) metallacycle complex. Coordination of HBpin to the intermediate would afford alkoxypinacolborane and regenerate Cp_2Ti(HBpin).

2.2. Zn Complex-Catalyzed Hydroboration of C=O. Umani-Ronchi and Cozzi et al. synthesized a bis(oxazoline) Zn(II) complex **2a** (Figure 2) and employed it in a catalytic hydroboration (10 mol %) of α-methoxyacetophenone at 0 °C, affording (*S*)-(+)-2-methoxy-1-phenylethanol (78% yield and

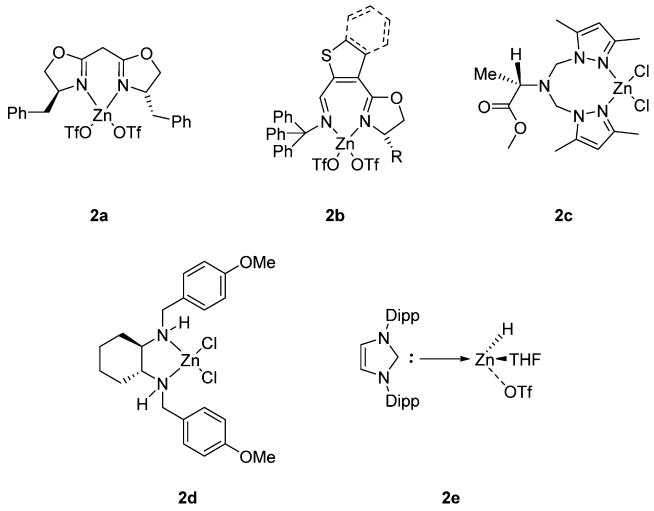
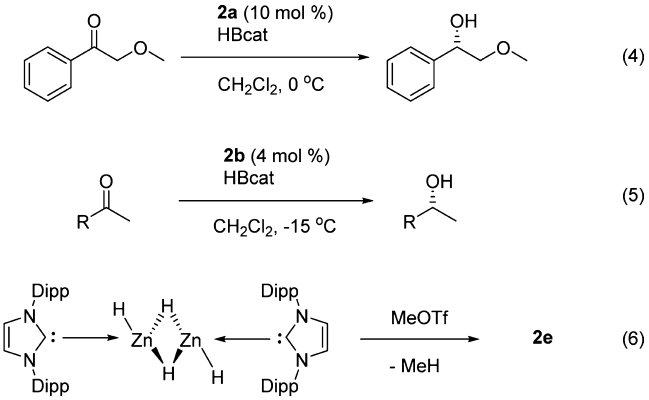


Figure 2. Zn complexes employed in reduction of ketones.

82% ee) (eq 4).[36] It was mentioned that a two-point binding site (thus, two O atoms of α-methoxyacetophenone) to Zn



center is required for high ee values, therefore restricting the ketone substrates only to α-alkoxyketone derivatives. To improve the enantioselectivity, Cozzi et al. developed the Zn(II) complex supported by an iminooxazoline (IMOX) ligand **2b** (Figure 2).[37] In a typical example of their work, IMOX ligand (0.024 mmol) and $Zn(OTf)_2$ (0.024 mmol) were mixed initially, followed by addition of freshly distilled ketones (0.6 mol) at −20 °C, and then HBcat (0.9 mol) was added dropwise. The reaction was placed in the freezer for 48 h at −15 °C (eq 5). A variety of ketones were reduced efficiently with good ee values (53% - 93%).

Separately, a pyrazole-based chiral L-alaninemethylester Zn(II) complex **2c** and a trans-1,-2-diaminocyclohexane derivative Zn(II) complex **2d** were developed by Kim and Jeong et al.[38,39] Both **2c** and **2d** were subjected to catalytic hydroboration of acetophenone using HBcat; however, low ee values (21% and 48%) of the corresponding alcohol were obtained.

A remarkable cationic Zn(II) monohydride complex used in hydroboration was briefly mentioned by Rivard and Brown et al. very recently.[40] Typically, Zn(II) hydrides are unstable and readily decompose. However, it can be stabilized by incorporation of donor ligands onto a Zn center. They synthesized a N-heterocyclic carbene (NHC)-stabilized zinc monohydride cation **2e** from the methylation of dimeric $[IPr{\cdot}ZnH(\mu\text{-}H)]_2$ (eq 6). Compound **2e** is effective for hydrosilylation of

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benzophenone, and a 0.1 mol % of **2e** catalyzes hydrosilylation of benzophenone at room temperature with a TOF of 475 h^{-1}. In this report, they briefly mentioned that the analogous hydroboration reactions can also performed using HBpin as the reductant and with a TOF of 1100 h^{-1}.

2.3. Shvo's Catalyst in Hydroboration Reactions. The Shvo's catalyst $[2,3,4,5\text{-}Ph_4(\eta^5\text{-}C_4COH)Ru(CO)_2H]_2$, **3a**, is a versatile catalyst in the hydrogenation of unsaturated bonds, such as alkenes, carbonyls, and imines (Figure 3).[41−44] The

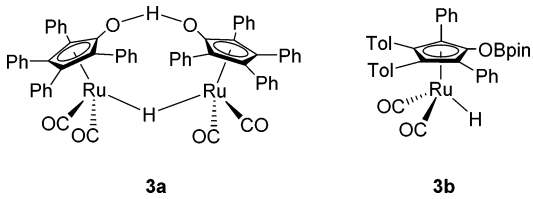
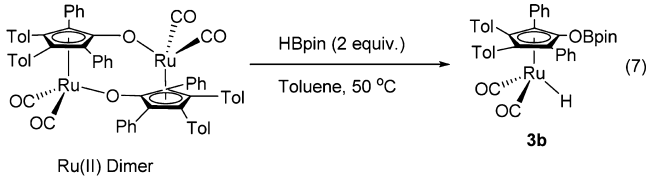
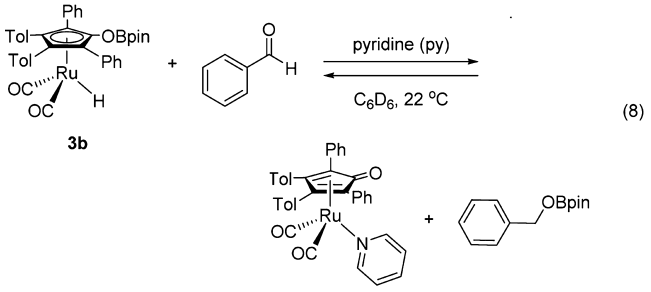
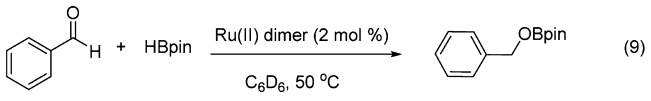


Figure 3. Shvo's catalyst **3a** and its boron derivative **3b**.

reaction mechanism for the hydrogenation process has been extensively studied.[45−52] In 2009, Casey and Clark et al. reported that the boron-substituted Shvo's catalyst **3b** was effective in the catalytic hydroboration of aldehydes, ketones, and imines (Figure 3).[53] Synthesis of **3b** was straightforward by adding HBpin (2 equiv) to Ru(II) dimer (1 equiv) at 50 °C for 2 h in toluene (eq 7). The ^1H NMR spectrum of **3b** showed a resonance at −9.33 ppm, confirming the presence of a Ru−H bond and implying the existence of monomeric **3b** in solution.

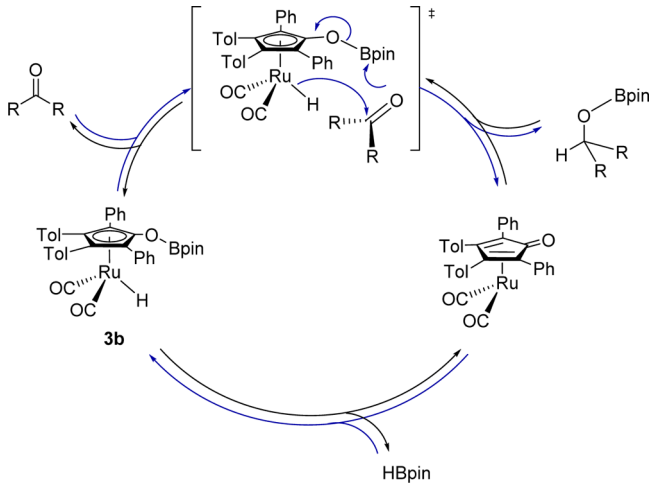






A stoichiometric reaction between **3b** and benzaldehyde , in the presence of pyridine as a trapping reagent produced the hydroborated product in 90% NMR yield after 1 h at 22 °C (eq 8). The reaction was then extended to catalytic conditions; thus, the Ru dimer precatalyst (2 mol %) and HBpin (1.5 equiv) yielded the corresponding hydroborated product in 99% after 21 h at 50 °C (eq 9). Various aldehydes containing electron-donating or electron-withdrawing groups were also examined and gave the products in good to excellent yields (60−91%). Similar to the case with **1d**, electron-deficient aldehydes reacted much faster than electron-rich counterparts. In addition, the hydroboration reaction was found to be reversible when the reaction period was extended up to 24 h. To elucidate the reaction mechanism, a Hammett plot for para-substituted benzaldehyde was drawn, and a reaction constant, ρ, of +0.91 (R^2 = 0.98) was estimated. The value of ρ is lower than that for reduction of benzaldehyde with an other reductant, such as $NaBH_4$ (+3.8), suggesting a decreased charge build-up in the transition state involving complex **3b**. The proposed reaction mechanism is shown in Scheme 4. The

Scheme 4. Proposed Catalytic Cycle for Hydroboration of Carbonyl Compounds Catalyzed by 3b



initial step involves a concerted transition state consisting of Ru−H, O-Bpin, and C═O moieties, which eventually affords the hydroborated product concomitant with the generation of coordinatively unsaturated Ru complex. The next step would be the regeneration of active catalytic species **3b** via addition of HBpin to the Ru intermediate. The reaction was also extended to imines and ketones but harsher reaction conditions were required therein. For instance, hydroboration of *N*-benzylideneaniline using Ru(II) dimer (4 mol %) afforded only 82% of the corresponding *N*-borylamine after 5 days at 70 °C, and hydroboration of acetophenone using Ru(II) dimer (4 mol %) afforded 50% of the hydroborylated product after 3 days at 70 °C.

3. GOLD COMPLEX-CATALYZED HYDROBORATION OF IMINE DERIVATIVES

Imines are easily accessible from the condensation reaction of carbonyl compounds and primary amines. Imines are also suitable precursors for the synthesis of secondary amines through reduction of the C═N bond. Similar to reduction of carbonyl compounds, the reduction of imines can be performed using metal hydride reagents such as $LiAlH_4$ or $NaBH_4$, yet these reagents usually result in poor yield and selectivity of the products.[54,55] Hence, the development of transition metal-catalyzed hydrogenation of C═N has been extensively explored.[56]

Catalytic hydroboration of imines can be considered an important synthetic route to reduce the C═N bond. The first transition metal-catalyzed imine hydroboration was reported by

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Baker and Westcott et al. in 1995.[57] They synthesized a variety of coinage metal (Cu, Ag, and Au) complexes, and $[AuCl(L)]_n$ **4a**−**c** (5 mol %) were found to be effective in the hydroboration of imines to give corresponding *N*-borylamines (Figure 4). Interestingly, the formation of small amounts of

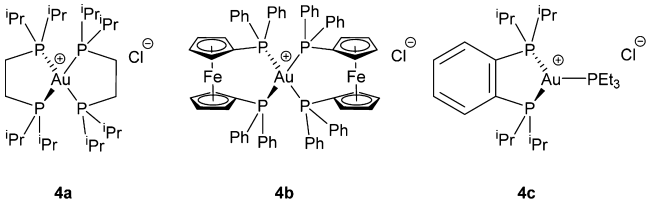
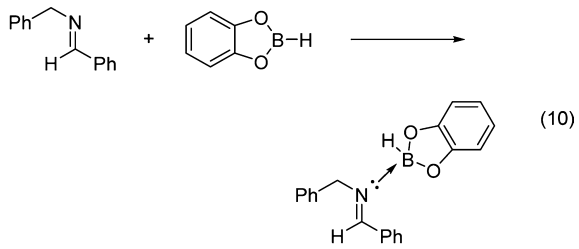
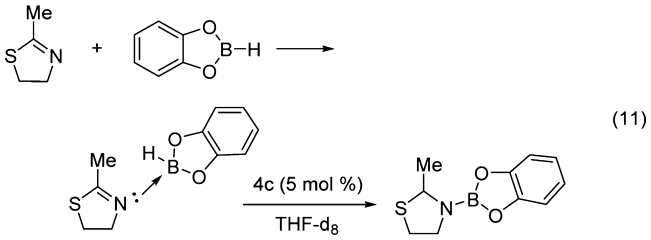


Figure 4. Au(I) complexes used in hydroboration of imines.

iminoborane adducts was observed upon addition of unhindered imines to HBcat (eq 10). Similarly, adducts with

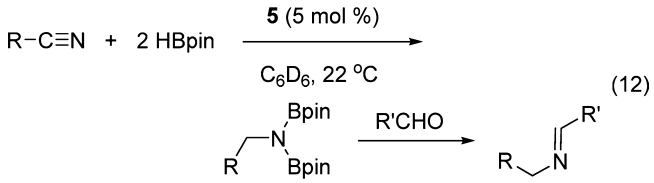




cyclic imines, 2-methyl-4,5-dihydrothiazole, were also observed, to which addition of Au complex **4c** produced the corresponding *N*-borylamine product (eq 11). Notably, no reactions were observed between Au complexes and HBcat, thereby ruling out the oxidative addition mechanism of the hydroboration. Instead, a plausible mechanism that involves the activation of iminoborane adduct by Au complexes (eq 11) was proposed.

4. MOLYBDENUM COMPLEX-CATALYZED HYDROBORATION OF UNSATURATED C−X BOND

Recently, Nikonov et al. developed an imidohydrido Mo(IV) complex **5** for catalytic hydroboration (Scheme 5).[58] Complex **5** has already been shown to catalyze the hydrosilylation of carbonyl as well as nitrile functional groups, which entails one of the few examples of nitrile hydrosilylation.[59,60] Nikonov et al. also conducted hydroboration on a variety of carbon-containing unsaturated bonds, including carbonyl derivatives, alkenes, alkynes, and nitriles. In a typical example, **5** (5 mol %), HBcat, and unsaturated substrate were mixed in C_6D_6 at 22 °C. Excellent yields were obtained for carbonyl (91−100%) and nitrile substrates (100% for both MeCN and PhCN). Remarkably, the hydroboration of nitriles resulted in a double addition of HBcat across C≡N moiety (eq 12). Note that the products from hydroboration of nitriles reacted with aldehydes readily to give imines (eq 12). This illustrates a useful methodology to synthesize imines from nitriles under mild conditions.



The reaction mechanism for the hydroboration of nitrile was investigated by stoichiometric reaction of **5a** with nitrile substrates. Complex **5a** was fully characterized by several spectroscopic methods, including X-ray diffraction, NMR, and IR spectra analyses. A stoichiometric reaction of **5a** with HBcat was monitored by low-temperature NMR spectroscopy ranging from −30 °C to room temperature. A mixture of two species (**5a**,**b**) was observed, and it was postulated that **5b** has an agostic borane structure containing bridging hydride (Scheme 5). Another intermediate, **5c**, was generated upon gradual increase in temperature and was proposed to contain a coordination of iminoborane to the Mo center. At 25 °C, both **5b** and **5c** disappeared concomitant with the formation of **5d**, which consists of a π-coordinated imine−borane complex. Further addition of HBcat would release the *N*-diborylamine product. Importantly, no oxidative addition products were observed in reacting HBcat with **5** or **5a**, indicating that oxidative addition mechanism could be deemed invalid.

Another Mo complexes capable of reducing C−X unsaturated bonds is the oxomolybdenum(VI) complexes, such as $CpMoO_2Cl$ or MoO_2Cl_2 **6** (Scheme 6). Among them, MoO_2Cl_2 **6** has been shown to catalyze hydrosilylation of carbonyl compounds, imines, amides, sulfoxides, and pyridine *N*-oxide.[61−65] The mechanistic studies on hydrosilylation using oxo-Mo complexes have been investigated, and DFT calculation supported the [2 + 2] addition mechanism as proposed by Toste et al.[66,67] On the contrary, few catalytic hydroborations by oxo-Mo complexes have been reported. Fernandes et al. reported the MoO_2Cl_2 (5 mol %)-catalyzed hydroboration of sulfoxides S=O with HBcat or BH_3·THF to yield sulfides.[68] A preliminary DFT calculation on this reaction was performed by Calhorda et al., who proposed a similar [2 + 2] addition mechanism.[69]

However, recent DFT (LanL2DZ for Mo and 6-311g(d,p) for the rest of the atoms) mechanistic studies by Wei et al. on catalytic hydroboration of ketone or aldehyde by MoO_2Cl_2 revealed an alternative ionic mechanism in addition to the conventional [2 + 2] addition mechanism.[70] A brief description of the [2 + 2] addition mechanism is summarized in Scheme 6. First, initial addition of HBcat across the Mo=O bond to form the Mo−H complex **6a** is proposed because the oxidative addition on the d^0 Mo(VI) center is unlikely to occur. Subsequent coordination of benzophenone followed by Mo−H hydride insertion into the C=O of the ketone in **6b** generates Mo alkoxide complex **6c**. The final step involves a retro [2 + 2] reaction to produce hydroborated product and regenerate oxo-Mo complex **6**. The free energy profile for each intermediate and transition state was theoretically determined, in which the [2 + 2] addition step was turnover-limiting, with an activation free energy barrier of +27.6 kcal mol^{-1}. On the other hand, the ionic mechanism (Scheme 7) was found to involve a similar activation barrier (26.9 kcal mol^{-1}), therefore suggesting that both the [2 + 2] addition pathway and the ionic pathway may be competitive. The initial step is the formation of an η^1-borane Mo complex, **6d**, which is followed by a coordination of the O atom in benzophenone to the B atom to form loosely

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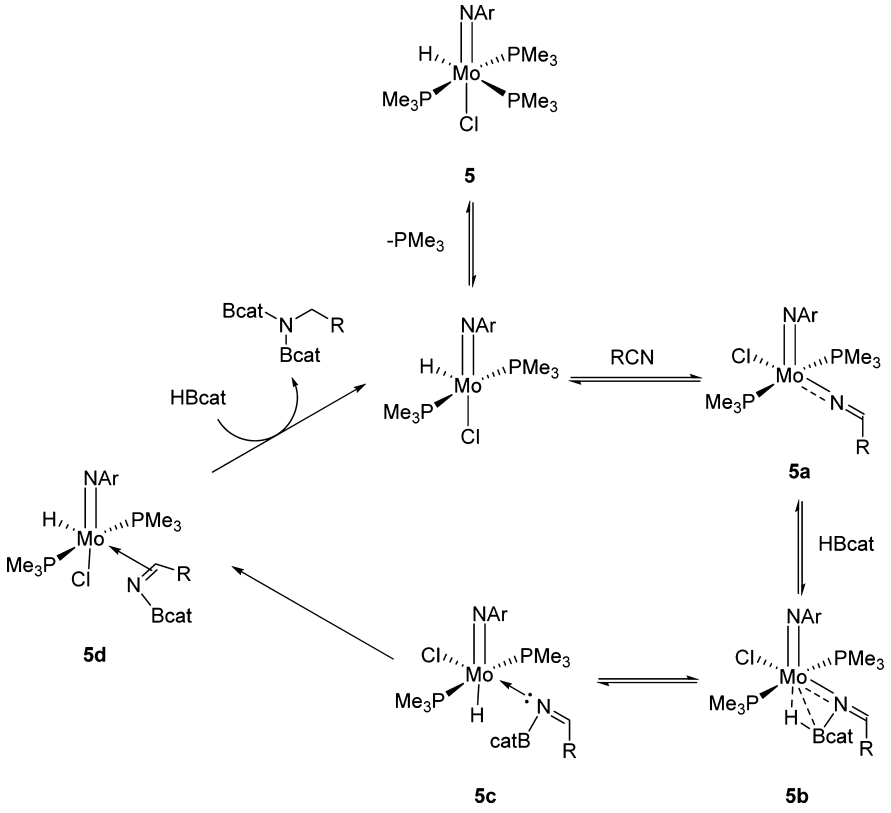
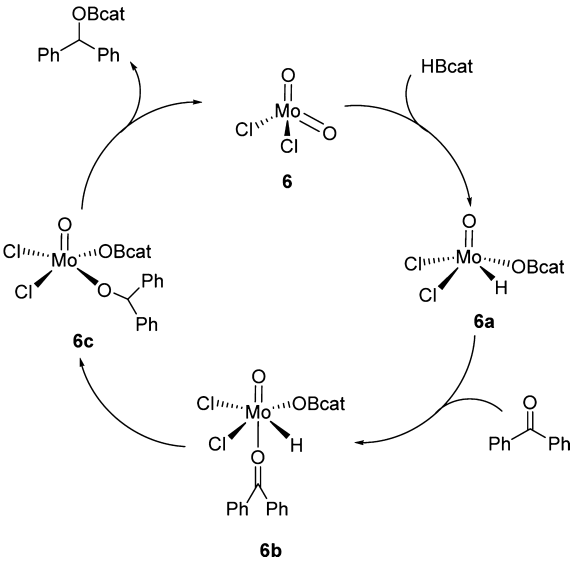
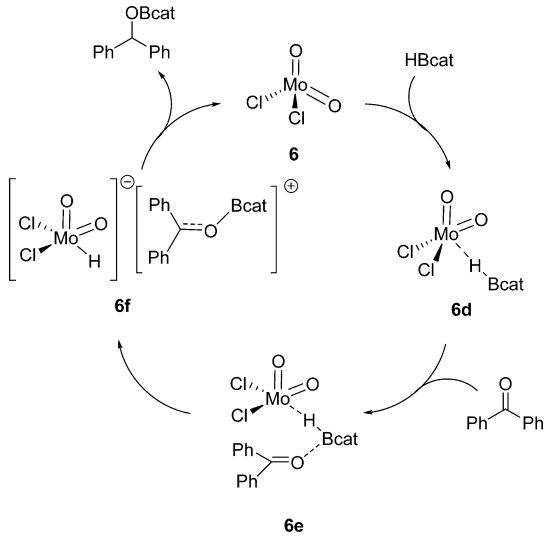
Scheme 5. Proposed Mechanism for Catalytic Hydroboration of Nitrile Using 5



Scheme 6. Postulated [2 + 2] Addition Pathway for Hydroboration of Ph_2CO Catalyzed by MoO_2Cl_2 Complex



Scheme 7. Alternative Ionic Mechanism for Hydroboration of Ph_2CO Using MoO_2Cl_2



bound adduct **6e**. Next, a heterolytic cleavage of the B−H bond would generate $(HMoCl_2O_2)(Ph_2COBcat)$ **6f**. A shift in the orientation of Mo−H complex would give rise to hydride abstraction by cationic $[Ph_2COBcat]^+$ to form $Ph_2CHOBcat$ and oxo-Mo(VI) catalyst **6**.

5. MAIN GROUP COMPOUNDS IN CATALYTIC HYDROBORATION REACTIONS

The field of main group chemistry has received the utmost attention over the past decade, mainly because of the ability of main group compounds to mimic transition metal complexes in small molecule activation and catalysis.[71−75] Particularly, recent developments of catalysis with main group compounds supports a possibility of replacing toxic and expensive transition metals with a less expensive and abundant p-block compound in various reactions. Given the vast number of reactions that main group compounds could participate in, here, we focus on their use as catalysts in hydroboration reactions. One of the well-known metal-free catalysts for hydroboration is the Corey−Bakashi−Shibata (CBS) catalyst, which is used for the asymmetric reduction of ketones.[76,77] The CBS catalyst can

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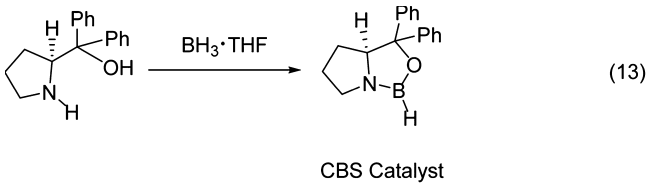
be synthesized from the reaction of diphenylproline with BH_3 (eq 13), and many other variations based on this catalyst have



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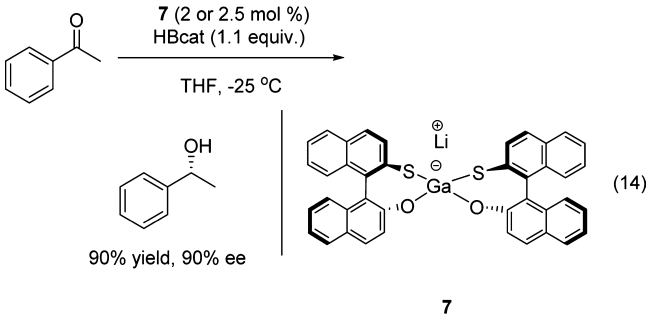
CBS Catalyst



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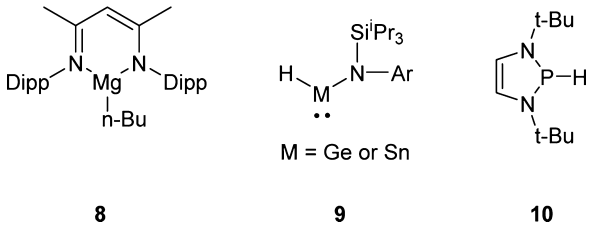
7

been synthesized in similar ways.[78] In addition, Woodward et al. reported the enantioselective reduction of prochiral ketones using LiGa(MTB)$_2$ **7**, generated in situ from the reaction of 2-hydroxy-2′-mercapto-1,1′-binaphthyl, (*R*)-(−)-$MTBH_2$ and $LiGaH_4$ (Figure 5).[79] In the catalytic reaction, **7** (2−2.5 mol %)



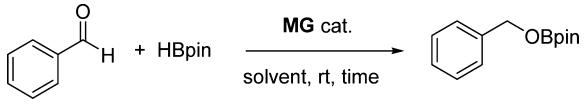
8 **9** **10**

Figure 5. Main group compounds utilized in hydroboration of aldehydes and ketones.

and ketone substrate were mixed in THF, followed by addition of HBcat (1.1 equiv) (eq 14). The reaction was conducted at −15 to −25 °C which produced the corresponding secondary alcohol in reasonable yields and ee values.

Recently, Hill, Jones, and our group have independently demonstrated the use of main group compounds (**8**−**10**) in hydroboration of ketones and aldehydes (Figure 5). Hill et al. employed (^{Dip}Nacnac)Mg^{n}Bu **8** [^{Dip}Nacnac = (DipNC-Me]$_2$CH$^-$, Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$) as a precatalyst for the hydroboration reaction (Scheme 8a).[80] The active catalyst in the catalytic cycle was determined to be a dimeric species, [(^{Dip}Nacnac)Mg^{n}H]$_2$, formed by reaction of HBpin with **8**. A catalytic amount of **8** (0.05−0.5 mol %) effectively promoted hydroboration of various aldehydes, including ferrocenecarboxyaldehyde and 3-pyridinecarboxylaldehyde, and products were obtained in excellent yields (93−>99% NMR yields) within hours (0.2−4.3 h) at room temperature. Similarly, 0.1−0.5 mol % of **8** could catalyze hydroboration of ketones to afford the corresponding hydroborated products in excellent yields (91−>99% NMR yields).

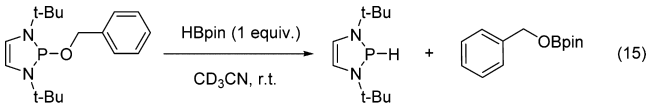
Scheme 8. Summary of Reaction Conditions for Benzaldehyde Hydroboration Using Main Group Catalysts Reported by (a) Hill, (b) Jones, and (c) Kinjo



[a]Hill: **8** (0.05 mol %), C_6D_6, 0.25 h, 95% NMR yield. [b]Jones: **9** (0.05 mol %), C_6D_6, 2.5 h, >99% NMR yield. [c]Kinjo: **10** (0.5 mol %), CD_3CN, 0.75 h, >99% NMR yield.

In 2014, Jones et al. reported hydroboration of a large number of aldehyde and ketone substrates using low valent Ge(II) and Sn(II) hydrides **9** (Scheme 8b).[81] The precatalyst **9** catalyzed hydroboration of aldehyde substrates tremendously; good TOF values (17−>13 300 h^{-1}) as well as excellent yields (>99% NMR yields) were achieved. Hydroboration of ketone substrates required a higher loading, 0.5−5 mol % of pre-catalyst, but still gave products in excellent yields (80−>99% NMR yields).

Recently, our group demonstrated the first metal-free catalytic hydroboration of carbonyl compounds. Thus, we employed 1,3,2-diazaphospholene **10** for the catalytic hydroboration of carbonyl compounds (Scheme 8c).[82] Compound **10** was originally synthesized by Gudat et al., and their pioneering work revealed the hydridic reactivity of P−H with carbonyl substrate, such as benzaldehyde and benzophenone.[83] Because we had background knowledge according to our previous work in catalytic transfer hydrogenation, **10** features the electrophilic P center, which could interact with a polar σ-bond of other substrates.[84] We confirmed that a stoichiometric addition of HBpin to benzyloxydiazaphospholene **10a** afforded hydroborated product and regenerated compound **10** (eq 15). In a typical example of aldehyde hydroboration,



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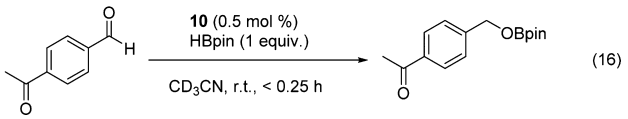
10a **10**



(16)

10 (0.5 mol %), HBpin (1 equiv) and aldehyde were mixed in CD_3CN at room temperature. Hydroborated aldehydes were obtained in good yields (70−>99%) with reasonable TOFs (19.6−>792 h^{-1}).

Although harsher reaction conditions (10 mol % **10**, 1.3 equiv of HBpin, 90 °C) were required, probably because of both steric and electronic factors, hydroboration of ketones was also achieved (98∼>99% NMR yield). It is noteworthy to mention that this result demonstrated the first phosphorus catalyst used in the hydroboration reaction. Significantly, when 4-acetylbenzaldehyde was employed, a selective hydroboration only at the aldehyde functional group was observed (eq 16) which had been previously unachievable. For comparison, catalytic hydroboration of benzaldehyde with **8**−**10** is summarized in Scheme 8.

5.1. σ-Bond Metathesis Mechanism. The mechanism of these reactions was explored separately. Hill et al. had previously isolated compound **8a** from the reaction of **8** with $PhSiH_3$ (eq 17),[85] which could be the active catalytic species in their catalytic system. Likewise, they also characterized

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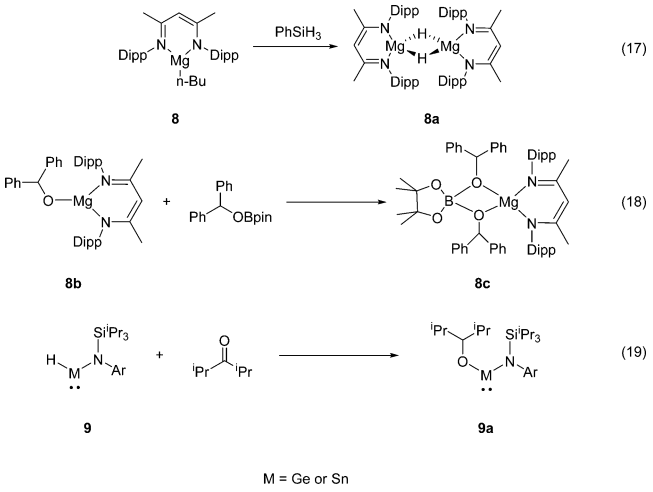

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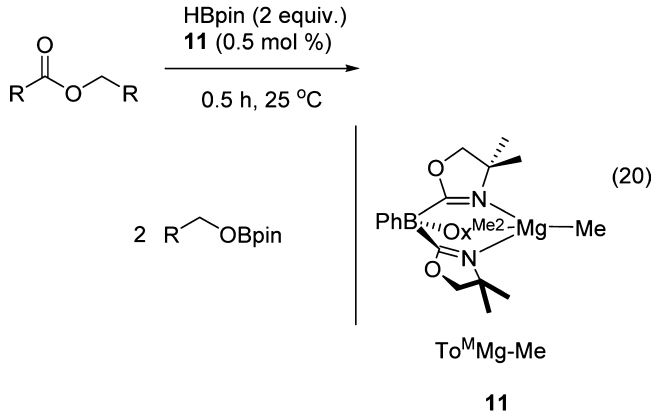
(19)

compound **8c** formed via a [2 + 2] interaction between Mg alkoxide **8b** and pinacolborate ester (eq 18). Jones et al. isolated the intermediate species, M-alkoxide complexes (M = Ge or Sn) **9a** by reaction of **9** with bulky carbonyl substrates ($^{i}Pr_2C$═O or (*p*-MeOPh)CHO) (eq 19). These stoichiometric reactions imply that insertion of M−H hydrides into C═O could be the common initial step in the catalytic cycles. A σ-bond metathesis in the following step with HBpin would give pinacolborate ester product and regenerate the catalyst (Scheme 9).

Further insights into the mechanism were provided by Jones's group and our group. A first-order dependence of the reaction in both HBpin and catalyst as well as zero-order dependence in ketones were confirmed. On the basis of these experimental results, it can be proposed that the alkoxide intermediates are the resting state of the catalytic cycles; therefore, the rate-determining step of the catalytic cycles is the σ-bond metathesis step involving HBpin and the alkoxide intermediate.

We also applied an Eyring plot to determine the thermodynamic parameters. Free energy change ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) for transition state at 298 K were found to be +25.1 kcal mol^{-1}, +13.0 kcal mol^{-1}, and −34.9 e.u., respectively. Intuitively, the negative $\Delta S^{\ddagger}$ value agrees with the formation of a four-membered σ-bond metathesis transition state. In addition, we conducted kinetic isotope effect (KIE) studies employing D-Bpin and Ph_2CO^{18} in which both give normal kinetic isotopic values [DKIE for D-Bpin/HBpin: 2.69; KIE O^{18}/O^{16} = 1.05; double KIE (O^{18}, BD/O^{16}, BH) = 2.96], suggesting that cleavage of B−H and P−O are involved in the rate-determining step. DFT studies at B3LYP-D3(SCF)/B2//B3LYP-D3/B1 level of theory supported the experimental data and verified a nearly concerted σ-bond metathesis mechanism.

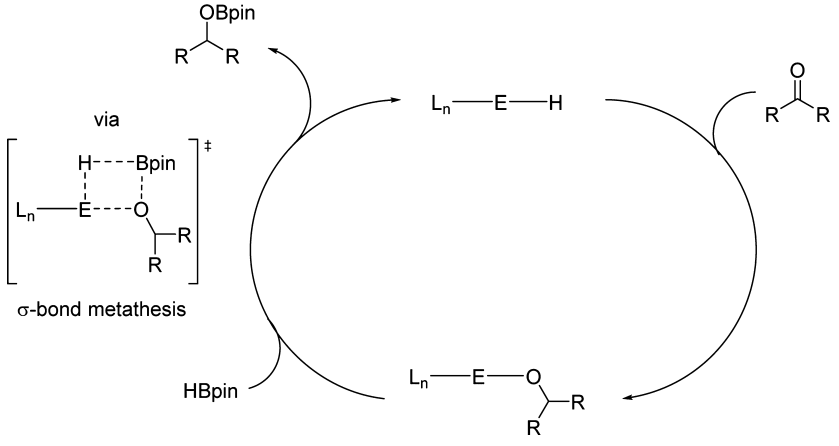
5.2. Zwitterionic Mechanism for Hydroboration of Esters. In addition to the σ-bond metathesis mechanism for main group-catalyzed hydroboration of C═O compounds, an alternative zwitterionic mechanism was proposed by Sadow et al.[86] Mg complex, To^{M}MgMe **11** (0.5 mol %), catalyzed hydroboration of esters with HBpin (2 equiv), giving rise to the corresponding alkoxyboronic acid pinacol ester (eq 20).



(20)

The conversion completed within 0.5−2 h for various ester substrates. Stoichiometric reactions confirmed that the reaction between **11** and HBpin is likely the initial step of the catalytic cycle that generates the To^{M}MgH$_2$Bpin intermediate. Interestingly, the reaction of **11** with HBpin was 20 times faster than that with EtOAc. Kinetic studies on the reaction using EtOAc as substrate were found to have first-order dependence in [**11**], half-order dependence in [EtOAc], and zero-order dependence in [HBpin]. Therefore, it can be concluded that the reactions of both **11** with EtOAc and **11** with HBpin are rate-limiting, which implies that σ-bond metathesis is not likely involved in the reaction mechanism. Further, a half-order dependence on [EtOAc] suggested a reversible Tischenko disproportionation, namely, formation of aldehydes from esters, in the reaction mechanism (Scheme 10). This was further evident by the successful cross-ester metathesis experiment in which two esters in a ratio of 1:1 were subjected to a catalytic amount of

Scheme 9. General σ-Bond Metathesis Mechanism for Hydroboration of Carbonyl Compounds



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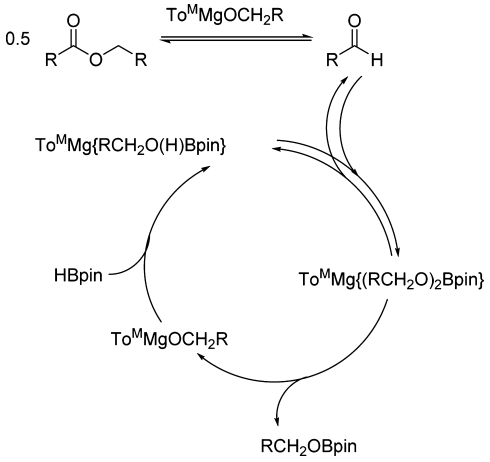
Scheme 10. Zwitterionic Mechanism for Hydroboration of Esters Proposed by Sadow et al.

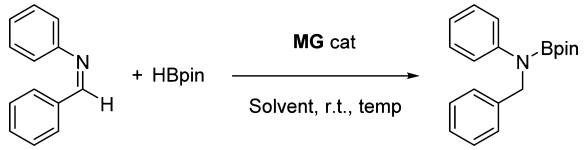


11 (10 mol %) to give the corresponding crossover products. NMR analysis of the reaction proposed that the resting state of the catalyst is To^{M}Mg{EtO(H)Bpin}, containing a Mg−O−B bridging interaction. In addition, they also ruled out any formation of Mg hydride species because the reaction could be conducted in CH_2Cl_2.

5.3. Mg Complex-Catalyzed Hydroboration of Imines.

Similar to transition metals, a few main group compounds catalyze the hydroboration of the C=N bond to give the corresponding *N*-borylamines. Hill et al. reported (^{Dip}Nacnac)-Mg^{n}Bu **8** is effective as a precatalyst for hydroboration of imines in addition to carbonyl derivatives.[87] For instance, **8** (5 mol %) could catalyze hydroboration of *N*-benzylideneaniline with HBpin to afford the corresponding *N*-borylamine quantitatively within 0.2 h at room temperature (Scheme 11a). Likewise, in

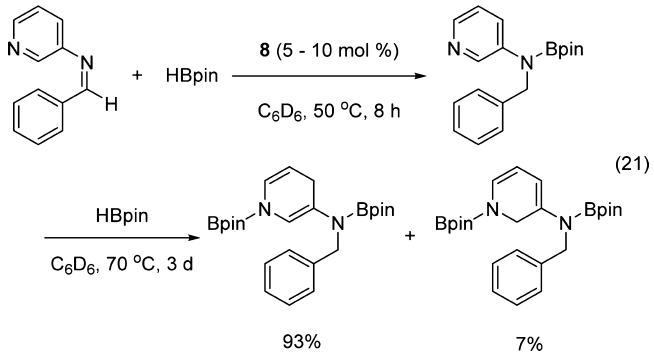
Scheme 11. Summary of Reaction Conditions for Hydroboration of *N*-Benzylideneaniline with Main Group Compounds Reported by (a) Hill and (b) Crudden



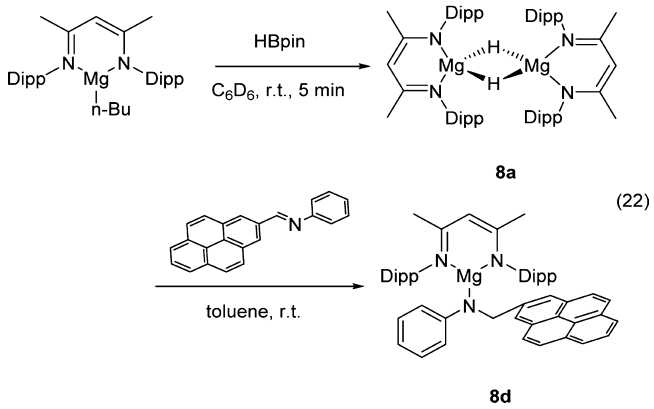
[a]Hill: **8** (5 mol %), C_6D_6, 0.2 h, >99% NMR yield. [b]Crudden: **12a** (5 mol %), $PhCF_3$, 1 h, 91% NMR yield **12b** (5 mol %), $PhCF_3$, 1 h, 100% NMR yield.

the case of ketones, a harsher condition was required for reduction of imines bearing secondary or tertiary alkyl substituents on the nitrogen atom. Hydroboration of pyridine substituted imine occurred only at the exocyclic imine moiety at 50 °C (eq 21). Interestingly, in the presence of another equivalent of HBpin and under increasing temperature (70 °C), 1,4-hydroboration of the pyridine moiety occurred (eq 21). The authors noted that competing catalyst deactivation took place at temperatures higher than 60 °C, resulting in poor yields for certain imine substrates.

The authors explored the mechanism of the imine hydroboration by stoichiometric reactions and kinetic studies. Stoichiometric reaction of **8** with HBpin and PhCH=NPh afforded *N*-borylamine product and also a small amount (~10%) of catalytically active species **8a**. Moreover, they



isolated the magnesium amide **8d** from the insertion reaction of Mg−H with (1-pyrenyl)CH=NPh at room temperature (eq 22). The initial insertion of Mg−H into imine was



concluded to be the rate-determining step. In fact, the reaction of **8** with HBpin (1 equiv) and bulky Ph_2C=NPh required heating at 50 °C for several hours.

Subsequent addition of another equivalent of HBpin led to rapid consumption of the magnesium amide intermediate and formation of the corresponding hydroborated product. Unlike the case of hydroboration of aldehyde or ketones, kinetic studies on this reaction exhibit a second-order dependence on imine, zero-order on HBpin, and first-order on catalyst. Therefore, the rate-determining step, imine precoordination and Mg−H insertion, is assisted by a second imine substrate through the displacement of HBpin from the Mg center.

5.4. Imine Hydroboration by Lewis Acid-Base Pair.

Recently, Crudden et al. reported the isolation of borenium salts and described their role in catalytic hydroboration of imines with HBpin.[88] The authors described that mixing $B(C_6F_5)_3$ and DABCO generates a Lewis acid−base adduct to which addition of HBpin afforded a borenium cation **12a** (eq 23). Another synthetic route to a similar borenium cation **12b** is through the reaction of Lewis acid−base adduct with HBpin in the presence of trityl salt $Ph_3C^+B(C_6F_5)_4^-$, which would abstract hydride from HBpin (eq 24).

Crudden et al. carried out catalytic hydroboration of imines at room temperature in the presence of **12a** or **12b** (5 mol %) in $PhCF_3$ (Scheme 11b). Importantly, catalytic activity of **12b**, which contains no hydride source, outperformed that of **12a** as determined kinetically by comparing reaction rates during conversion of Ph_2C=NCH_2Ph to the corresponding *N*-borylamine product. Hence, it was concluded that the mechanism did not follow the conventional mechanism

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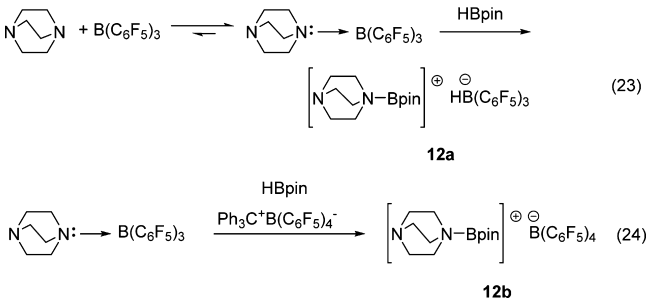
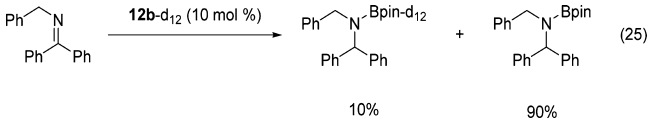
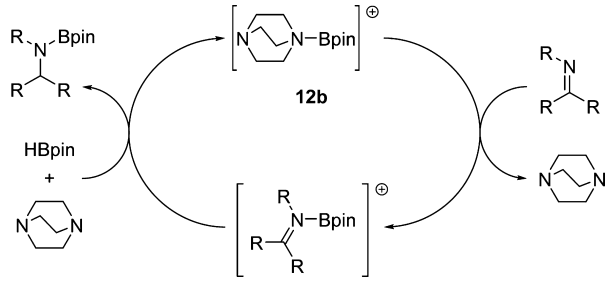


analogous to a frustrated Lewis pair (FLP)-mediated hydrogenation reaction.[89−92] A relatively high DKIE of k_H/k_D = +6.7 ± 0.1 was observed for reduction with H-Bpin and D-Bpin, indicating that the B−H bond activation participates in the rate-determining step. This is further supported by kinetic studies in which H-Bpin displayed a first-order dependency. Crudden et al. also observed the corresponding d_{12}-labeled product together with the normal product in a 1:10 ratio when employing perdeuterated borenium **12b**-d_{12} as catalyst (eq 25).



This result indicated that the borenium cation is transferred to the imine and regenerated after hydride transfer from H-Bpin. In accordance with these experimental observations, the mechanism in Scheme 12 was proposed.

Scheme 12. Hydroboration of Imines Catalyzed by Borenium Cation 12

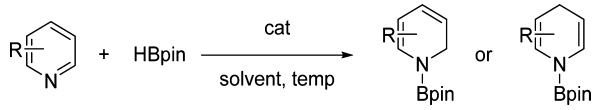


6. DEAROMATIZATION OF PYRIDINE THROUGH HYDROBORATION

Semiunsaturated heterocyclic compounds, such as 1,2-dihydropyridine derivatives have been of paramount importance in myriad fields of chemistry. For example, Hantzsch esters are important precursors for the synthesis of nicotinamide adenine dinucleotide (NADH) derivatives.[93−98] Moreover, 1,2-dihydropyridine derivatives are common components found in natural products as well as pharmaceutical drugs.[99−103] The selective dearomatization of nitrogen-containing heterocycles with alkali metals, such as MgH_2, is one of the most straightforward methods to produce semiunsaturated heterocycles; however, it requires harsh conditions and, hence, affects reaction selectivity.[104]

In advance of achieving hydroboration of imines and carbonyl substrates, Hill et al. reported catalytic hydroboration of pyridine derivatives with (^{Dip}Nacnac)Mg^{n}Bu **8** (5−10 mol %)

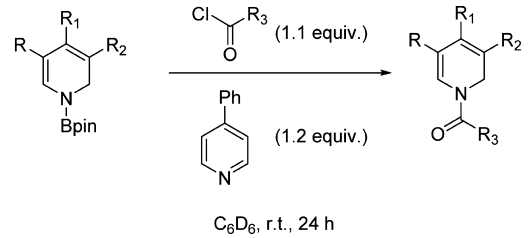
Scheme 13. Summary of Reaction Conditions for Hydroboration of Pyridine Derivatives Reported by (a) Hill, (b) Suginome, (c) Marks, and (d) Harder

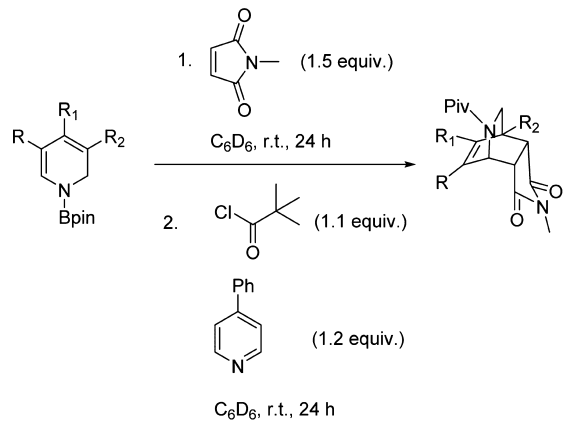


[a]Hill: **8** (5−10 mol %), C_6D_6, 25−70 °C, 3-21 h. [b]Suginome: $[RhCl(cod)]_2$ (1 mol %), PCy_3 (4 mol %), toluene, 50 °C, 24 h. [c]Marks: **13** (1 mol %), C_6D_6 or C_6D_{12}, 25−35 °C, 0.2−21 h. [d]Harder: **14** (5−10 mol %), C_6D_6, 25−60 °C, 1−48 h.

(Scheme 13a).[105] A mixture of 1,2- and 1,4-dihydropyridine was obtained, depending on the pyridine substrate. With 4-phenylpyridine, quinoline, and isoquinoline, only the 1,2-hydroboration products were obtained in reasonable yields (51−99% NMR yield). As expected, aldehyde, ester, and nitrile functional groups were not tolerated in their catalytic system. The proposed reaction mechanism for this catalytic cycle was similar to the σ-bond metathesis pathway depicted in Scheme 10.

Ohmura and Suginome et al. conducted similar hydroboration of pyridine using a Rh catalyst (Scheme 13b).[106] They found that use of the PCy_3 ligand (P/Rh = 2) provided the most effective combination for 1,2-hydroboration of pyridine. Thus, with $[RhCl(cod)]_2$ (1 mol %) and PCy_3 (4 mol %), hydroborated pyridines were obtained in 93% yield with a 98:2 ratio of 1,2- and 1,4-hydroborated pyridines. Pyridine substrates bearing electron-donating and electron-withdrawing groups were tolerated and gave the products in reasonable yields (58−96%). Interestingly, they also demonstrated a series of reactions, including acylation (eq 26) and the Diels−Alder reaction (eq 27) utilizing *N*-boryl-1,2-dihydropyridine as the





building block. The mechanism of the reaction was proposed to follow a similar mechanism based on catalytic hydroboration of alkynes and alkenes (Scheme 14).

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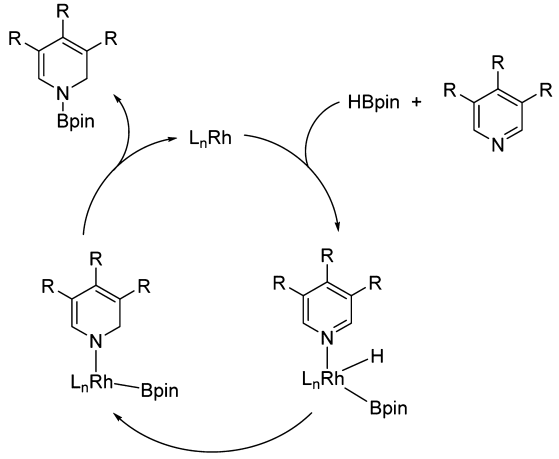
Scheme 14. General Mechanism for the 1,2-Hydroboration of Pyridine Substrates

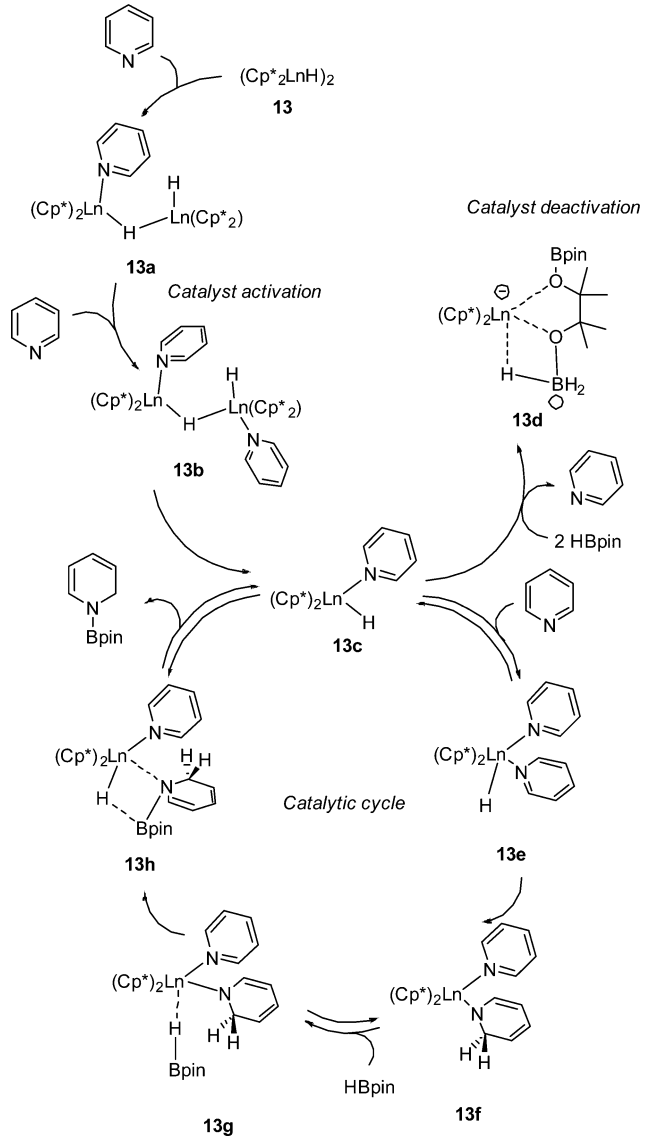


In 2014, Delferro and Marks et al. developed regioselective 1,2-hydroboration of functionalized pyridines catalyzed by organolanthanide catalyst $(Cp^*_2LaH)_2$ **13** (Scheme 13c).[107] Advantages of this catalytic system include the use of earth abundant lanthanide complex, presenting low toxicity as well as low cost, low catalytic loading (1 mol %), mild conditions employed (25−35 °C), and being atom-economical. Moreover, pyridine substrates with several functional groups were well-tolerated. To explore the reaction mechanism, kinetic studies were performed. It was revealed that a first-order dependence on [pyridine] was observed for concentrations below 0.2 M, whereas zero order was observed at higher [pyridine]. In addition, inverse first order with respect to HBpin was observed. Thus, the resting state of the catalyst would involve a pyridine-coordinated $Cp^*_2LaH(py)_n$ species and the intramolecular C═N insertion seems to be the rate-determining step. The inverse first order of [HBpin] suggests deactivating processes in the catalytic system. Kinetic measurement using Eyring and Arrhenius plots gave thermodynamic parameters as follows: $\Delta H^{\ddagger}$ = 15.7 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −27.2 ± 0.3 cal mol^{-1}, and E_a = 16.3 ± 0.4 kcal mol^{-1}.

DFT calculations at the M06/6-31G** level of theory and energetic span model were performed to gain deep insight into the catalytic cycle. It was found that the catalytic activation path involves the reaction of $(Cp^*_2LaH)_2$ with pyridine, giving rise to complexes **13a** and **13b** (Scheme 15). This step is followed by the dissociation of complex **13b** to generate active catalyst **13c**. The overall energy barrier of 7.6 kcal mol^{-1} is consistent with their experimental observation of rapid reaction between $(Cp^*_2LaH)_2$ and pyridine. The catalyst deactivation by HBpin was probed, and zwitterionic complex **13d** was isolated and characterized spectroscopically. Computationally, it was found that deactivation is favorable, with ΔG = −15.0 kcal mol^{-1}, and a barrier of 25.6 kcal mol^{-1} is accessible under the reaction conditions.

The proposed mechanism for pyridine dearomatization is depicted in Scheme 15. First, the authors explored the reaction mechanism, focusing on only one pyridine moiety on the Ln metal center in $Cp^*_2LnH(py)$ **13c**; however, a relatively large energetic span was obtained. Conversely, a further coordination of another pyridine molecule generating $Cp^*_2LnH(py)_2$ **13e** was found to be kinetically favorable (ΔG = +0.6 kcal mol^{-1}) and also gave a lower energy span upon intramolecular hydride insertion into the C═N of the pyridine to give **13f**.

Scheme 15. Mechanism for Selective 1,2-Hydroboration of Pyridine Catalyzed by $[Cp^*_2LnH]_2$



Subsequently, HBpin would coordinate to the Ln center to form **13g**, which then undergoes a fast and concerted σ-bond metathesis via a four-membered transition state to yield a stable complex **13h**. Elimination of the 1,2-hydroborated pyridine moiety would regenerate the active catalyst **13c** and complete the catalytic cycle.

Harder et al. reported another catalytic hydroboration of pyridines with Mg hydride tetramer **14** as the catalyst (Scheme 13d).[108] Addition of pyridine (8 equiv) to the tetranuclear magnesium cluster **14** induced a hydride transfer to the 2-position of the pyridine ring (eq 28).

Importantly, the resulting product is stable and does not undergo rearrangement to form 1,4-dihydropyridine, even with prolonged heating at high temperatures. Such stability might originate from C−H···C π interactions between the CH_2 group and the Dipp group. Meanwhile, under catalytic conditions, **14** (10 mol %) afforded the corresponding dihydropyridine as a 24:76 mixture of 1,2- and 1,4-hydroborated products (Scheme 13). The stoichiometric reaction was thus not in line with that conducted in catalytic scale. These discrepancies can

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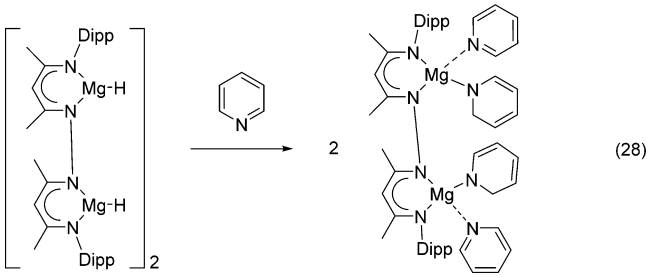
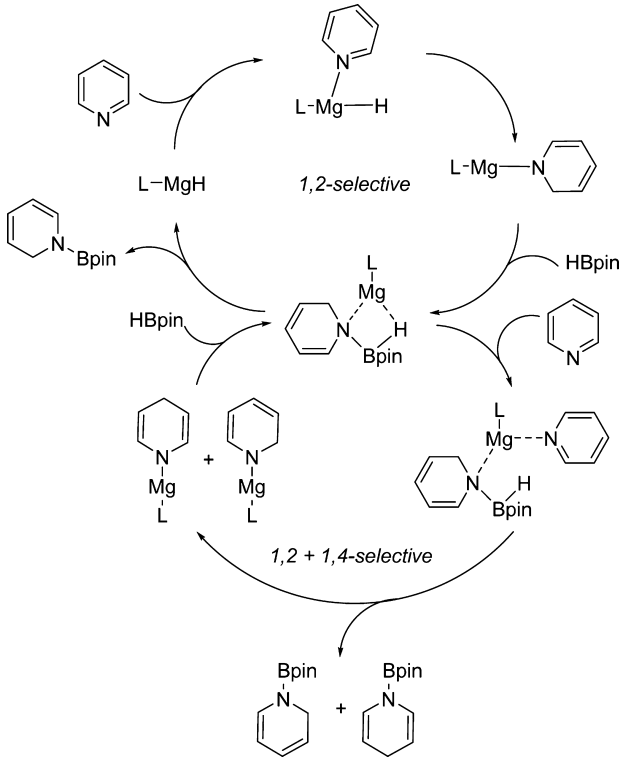


14

be attributed to several features of the complex. As the authors pointed out, the heteroleptic nature of **14** would render stability of the complex toward ligand exchange process and formation of homoleptic complex and MgH_2. The system would be nonselective if MgH_2, generated by Schlenk equilibria, were the active catalyst. However, they did not observe any indication for such mechanism, and therefore, a nonselective hydroboration pathway as summarized in Scheme 16 was proposed.

Scheme 16. Alternative Mechanism for Non-Selective Hydroboration of Pyridines Catalyzed by LMgH Complex

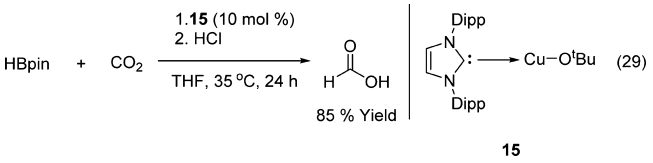


7. REDUCTION OF CO_2 THROUGH HYDROBORATION

Reduction and transformation of carbon dioxide (CO_2), recognized as one of the greenhouse gases, have received considerable attention because CO_2 is an inexpensive carbon source, nontoxic, and nonflammable.[109−111] Notably, reduction of CO_2 could provide several compounds, such as methanol, carbon monoxide, from reverse water−gas shift reaction (WGSR), formaldehyde, formic acid, or even methane.[112] Hydroboration of CO_2 is one of the useful methodologies for reducing CO_2, and several systems including both transition metals and main group elements have been shown to be effective in catalytic hydroboration of CO_2. This chapter provides an overview on the hydroboration of CO_2, and the reaction mechanism will be discussed in depth.

7.1. Transition Metal Catalyzed Hydroboration of CO_2.

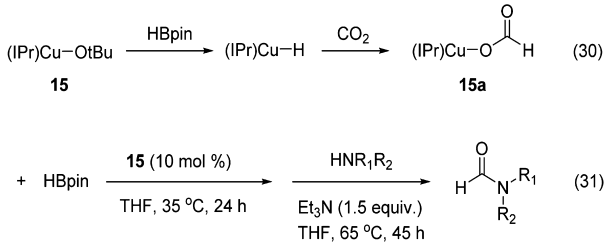
In 2013, Nozaki et al. reported reduction of CO_2 with HBpin catalyzed by N-heterocyclic carbene supported Cu(I) complex, (IPr)Cu(O^{t}Bu), **15**.[113] A catalytic amount of **15** (10 mol %) effectively promoted hydroboration of CO_2 (1 atm) in THF at 35 °C, and formic acid was obtained in 85% yield within 24 h (eq 29). The reaction was effective with lower catalytic loading



15

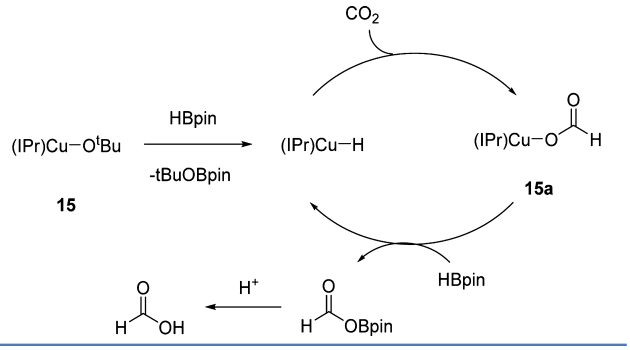
(5 mol %) or in other solvents, such as benzene. However, the reaction did not proceed when HBcat was used.

To investigate the reaction mechanism, stoichiometric reactions were conducted. The reaction of **15** with HBpin instantaneously generated thermally unstable (IPr)CuH. Subsequently, treatment of (IPr)CuH with CO_2 gave (IPr)-Cu(O_2CH) **15a** (eq 30). The authors synthesized **15a**



separately from the reaction of (IPr)CuH and Ag(O_2CH) and confirmed that **15a** could catalyze hydroboration of CO_2 to give formic acid in high yield (91%). On the basis of these studies, the reaction mechanism was proposed (Scheme 17).

Scheme 17. Cu(I) Mediated Hydroboration of CO_2



Interestingly, they discovered that the reaction product, HCO_2Bpin, can be directly used as formylation reagent with amines (eq 31). Both primary and secondary amines could give the corresponding formamides in good yields (81−98%). Conveniently, the reaction could also be conducted in a one-pot manner in which HCO_2Bpin was not isolated.

Guan et al. employed Ni(II) hydride POCOP-pincer complex, **16** (0.2 mol %), for the catalytic hydroboration of CO_2, which

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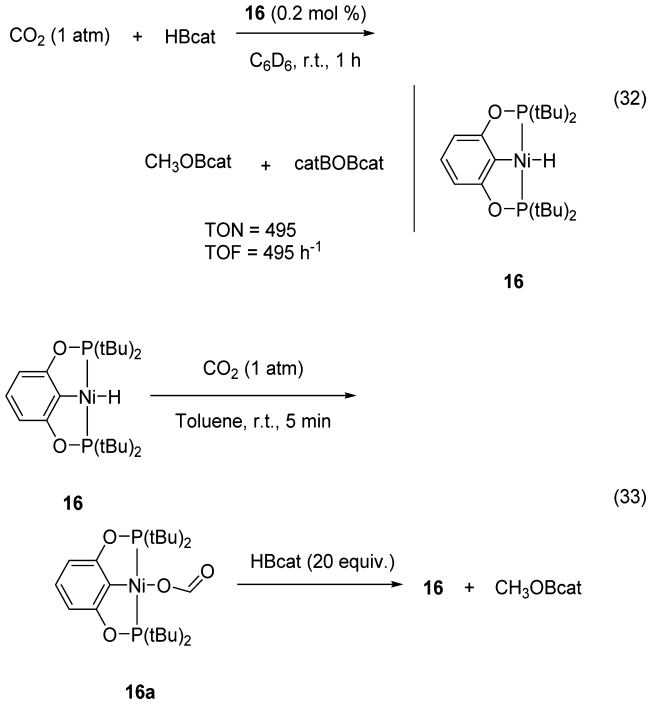
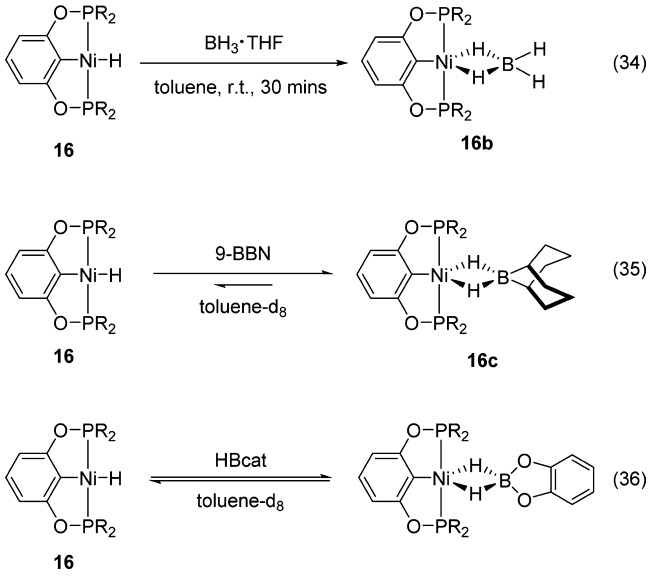


yields a TON of 495 (eq 32).[114] Similar to Nozaki's result, the stoichiometric reaction of **16** and CO_2 resulted in the formation of Ni(II) formate complex **16a** (eq 33). Interestingly, CO_2 insertion is reversible, as confirmed by the labeling experiments with $^{13}CO_2$. To regenerate the hydride complex **16**, HBcat (1 equiv) was added, which presumably yielded HCOOBcat. When excess HBcat was added (20 equiv), a new product was formed, which was assigned to CH_3OBcat (eq 33).

Guan et al. also studied the effect of the pincer ligand on Ni complexes extensively.[115] Interestingly, with bulky groups on the ligand (R = ^{t}Bu) the catalytic reaction proceeded faster (formation of CH_3OBcat within 45 min) than those having a relatively less bulky substituent (R = ^{i}Pr). In addition, several reducing agents were screened. 9-BBN and HBcat gave similar behavior, but only HCOOBpin was formed, even if an excess amount of HBpin was used. With $PhSiH_3$, in contrast, no reduction products of CO_2 were produced, even after 48 h.

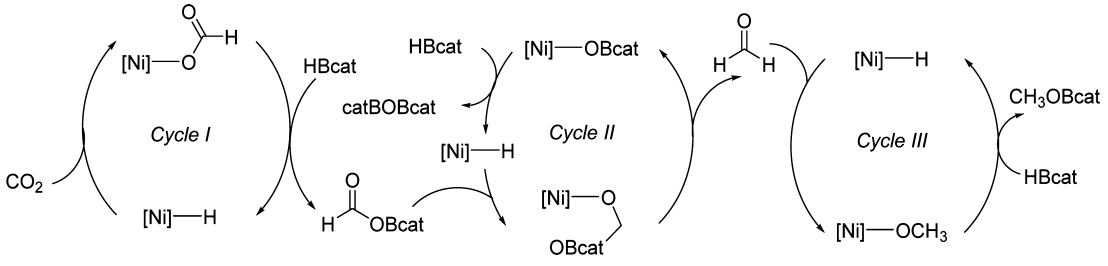
Further studies on the reactivity of **16** with various boranes were performed.[116] Significantly, the formation of borohydride complex **16b** was observed in reacting **16** (R = ^{t}Bu, ^{i}Pr, ^{c}Pe) with BH_3·THF (eq 34). The reaction completed within 30 min at room temperature. The formation of borane complex **16c** using 9-BBN was accomplished using **16** possessing less bulky substituent (R = ^{i}Pr), and it was found that **16** (R = ^{i}Pr) and



16c are in equilibrium, on the basis of variable temperature NMR analysis (eq 35) with a K_{eq} = 13.1 ± 4.5 $M^{-1/2}$ at 22 °C. The reaction of HBcat and **16** presumably afforded a borane complex, but a rapid equilibrium was established between them even at −70 °C (eq 36). The formation of these Ni borohydride complexes plays a crucial role in hydroboration of CO_2. Guan et al. also confirmed that the use of BH_3.THF as the reductant for the reduction of CO_2 shut down the catalytic activity at room temperature. This can be rationalized by the fact that the Ni−H complex **16** was trapped as borohydride complex and thus deactivated, as shown previously (eq 34). In contrast, the use of 9-BBN or HBcat retained catalytic activity when **16** (R = ^{t}Bu) was employed. This is because of the weaker interaction between active catalyst **16** and 9-BBN or HBcat.

To further understand the reaction mechanism, DFT studies were conducted in depth, and the proposed mechanism is summarized in Scheme 18.[117] The mechanism involves three cycles. The first cycle (cycle I) involves the insertion of [Ni]−H into a one of the C═O bonds in CO_2, which has a small barrier of 19.0 kcal mol^{-1}. Next, the reaction of [Ni]−formate complex with HBcat would go through two transition states with reasonable barriers of +22.6 and 23.0 kcal mol^{-1}, which regenerate [Ni]−H along with formation of HCOOBcat. The next cycle (cycle II) would involve an insertion of [Ni]−H into HCOOBcat, giving rise to formaldehyde. It has been shown that formation of formaldehyde was catalyzed by the Ni−H complex with significantly lower barrier (+32.5 kcal mol^{-1}) in comparison with the uncatalyzed reaction between HBcat and HCOOBcat (+43.6 kcal mol^{-1}). Finally, [Ni]−H would insert into CH_2O,

Scheme 18. Mechanistic Cycles for Ni−H Pincer Complex-Catalyzed Hydroboration of CO_2



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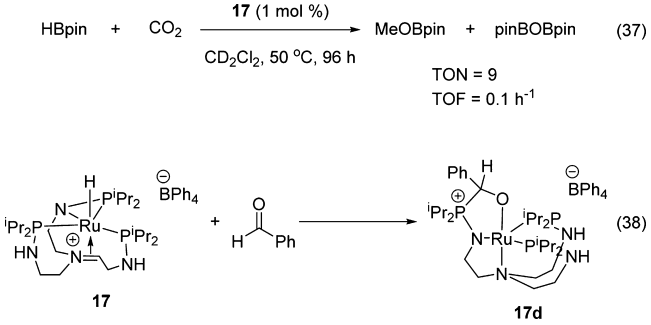
and subsequent metathesis affords CH_3OBcat (cycle III), which has the highest barrier of only 23.0 kcal mol^{-1}.

Ru complexes have also shown activity in catalytic hydroboration of CO_2. In 2012, Stephan et al. developed a Lewis acidic Ru cationic complex **17** containing phosphine donor ligands;[118] thus, it was deemed chemically similar to that of frustrated Lewis pairs. Stoichiometric reaction of **17** with CO_2 afforded the novel phosphonium adduct **17a** in good yields (81%), with concomitant transfer of the Ru hydride to the ligand's iminium carbon. Subsequent addition of HBpin (5 equiv) to **17a** gave MeOBpin after 24 h, as monitored by NMR spectroscopy. The catalytic reaction was also investigated using **17** (5.6 mol %) and HBpin. The reaction mixture was heated at 50 °C under 1 atm of CO_2, and 75% of HBpin was consumed after 96 h, giving MeOBpin and pinBOBpin. With 1 mol % of **17**, the TON increased to 9 after 96 h (eq 37). The authors noted that increasing the CO_2 pressure and using HBcat or 9-BBN had negligible effect on the rate of reaction or distribution of the hydroborated products.



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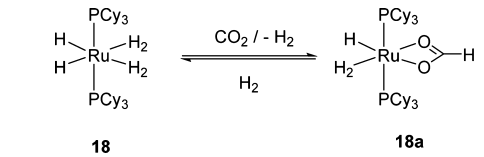
(38)

The reaction mechanism was examined by $^{13}CO_2$-labeled studies, and the proposed catalytic cycle is shown in Scheme 19. The reduction of **17** with HBpin in the presence of CO_2 formed a monohydroborated intermediate **17b**, which was fully converted to **17c** after 24 h. A compound **17d**, structurally similar to **17c**, was separately prepared from the reaction of **17** with benzaldehyde (eq 38). The authors confirmed that reaction of **17d** with HBpin generated hydroborated product $PhCH_2OBpin$ when heated to 50 °C for 24 h. Thus, **17d** also catalyzed reduction of CO_2 (1 atm) in the presence of HBpin.

Sabo-Etienne et al. reported reduction of CO_2 by Ru complex $[RuH_2(H_2)_2(PCy_3)_2]$, **18**.[119] Stoichiometric reaction of **18** with CO_2 formed **18a**, whereas the reverse reaction using H_2 is also possible (eq 39). Reaction of **18** (10 mol %) and HBpin proceeds readily in the presence of $^{13}CO_2$ (1 atm) to give products **A**–**E** (eq 40). Mechanistic studies revealed the end products of Ru complexes **18b**–**e** (Figure 6) were in different proportions, depending on the catalyst loading. Interestingly, **18b** also displayed catalytic activity similar to that of **18** or **18a**. Stoichiometric reaction of **18b** with HBpin afforded Ru complex **18d** and products **A**, **B**, and **D** (eq 41). Further exposure of CO_2 to **18d** resulted in regeneration of complex **18b** concomitant with the formation of **A**, **B**, and also **C**, which was previously not observed from reaction of **18b** with HBpin (eq 42).

Further investigation into the mechanism suggested the formation of formaldehyde (CH_2O) in the reaction.[120] Thus, addition of CH_2O to the reaction mixture resulted in the formation of compound **E** via reaction of CH_2O with **C** (eq 43). Moreover, it was found that the reaction of **C** with CH_2O proceeds even without the presence of any Ru catalyst.



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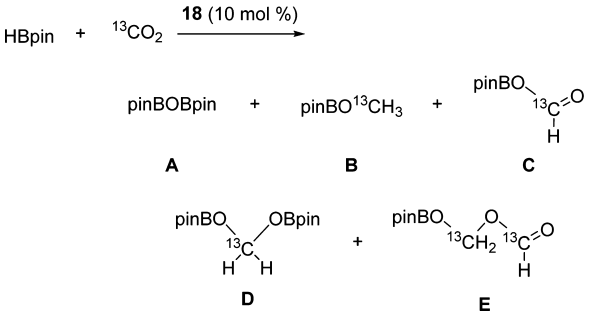

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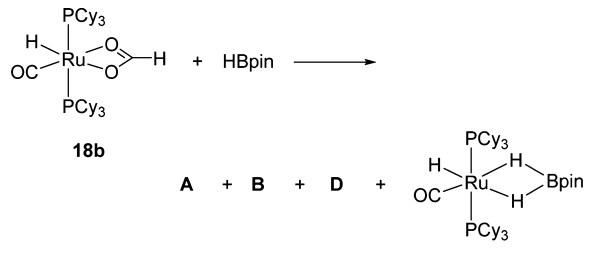

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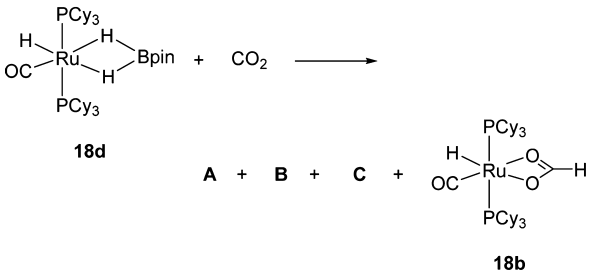

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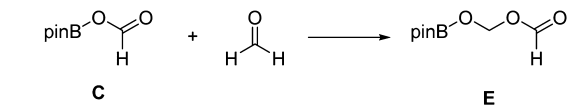

(43)

With Ru complex **19** replacing PCy_3 ligands with $PCyp_3$ (Cyp = cyclopentyl) in **18**, formation of free formaldehyde was observed in the catalytic reaction (Figure 7).[121] In addition, **19** displayed a higher catalytic activity than complex **18**. Significantly, no formation of **C** was observed because of the full conversion to **E** by a larger proportion of CH_2O. Compound **B** could also react with CH_2O to give **F** and **G** (eq 44). Low CO_2 pressure favors selective formation of CH_2O, and high CO_2 pressure or using THF as the solvent favors the formation of compound **C**.

The stark contrast between the reactivity of **18** and **19** can be attributed to the different Ru(II) products formed at the end of the reaction, in which complexes **19a**–**d** were observed (Figure 7). The enhanced catalytic activity was probably a result of the formation of complex **19b**, which was not observed in the system using complex **18**. The reaction mechanism was

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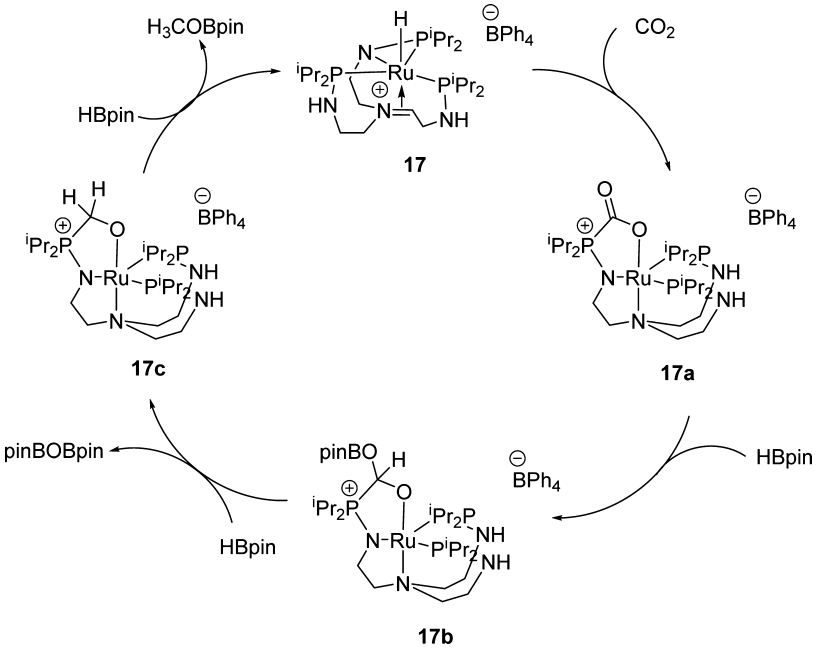
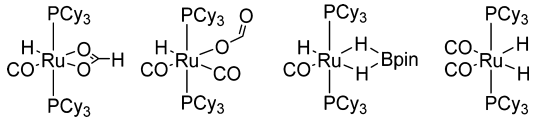
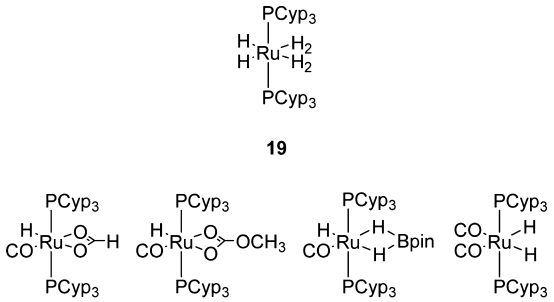
Scheme 19. Mechanism for Catalytic Hydroboration of CO_2 Using Ru(II) Complex 17





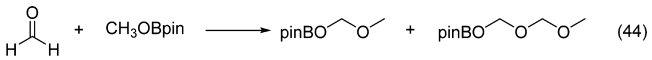
18b 18c 18d 18e

Figure 6. Ru(II) species observed in catalytic hydroboration of CO_2 using **18**.



19 19a 19b 19c 19d

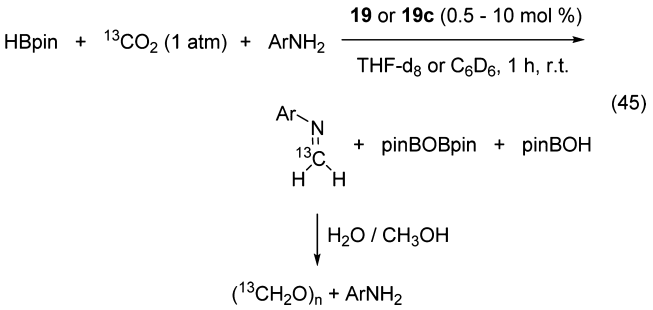
Figure 7. Ru(II) species observed in catalytic hydroboration of CO_2 using **19**.



B F G (44)

proposed, which involves three cycles (Scheme 20), similar to that reported by Guan et al. in Scheme 18.

Sabo-Etienne et al. also demonstrated the use of the amine function, such as 2,6-bis(diisopropyl)aniline ($DippNH_2$) as a trapping reagent for formaldehyde to form methylene aniline (eq 43). ^{13}C-labeled studies in a catalytic reaction with anilines showed full consumption of HBpin, and only ^{13}C-labeled methylene aniline product was observed. Hydrolysis of the methylene aniline product regenerated formalin solution and the aniline (eq 45).



(45)

In 2014, Hazari et al. described a Pd−H complex that could promote hydroboration of CO_2.[122] Initially, Pd complex **20** was employed for the carboxylation of allenes using CO_2. The presence of reductant such as $AlEt_3$ deactivated the catalyst; therefore, a milder reduction agent, HBpin, was sought. Instead of forming allene carboxylation product, a CO_2-hydroborated product HCOOBpin was observed (eq 46). Pd complex **20** displayed a high activity, with a TON of 63500. In addition, the reaction was highly selective because only HCOOBpin was observed as the major product (90%), in contrast to the case of Ru catalysts **18** and **19**. Similar to that for (IPr)Cu−H catalyzed hydroboration of CO_2 (Scheme 17), the proposed mechanism involves Pd−H insertion into CO_2, followed by σ-bond metathesis to regenerate **20**.

7.2. Main Group-Catalyzed Hydroboration of CO_2. Main group compounds such as FLPs and Lewis acidic species have been used in stoichiometric reduction of CO_2.[123−135] However, catalytic hydroboration of CO_2 using main group compounds has been rarely explored as compared wtih those transition metal catalysts as aforementioned. The first pioneering work on the hydroboration of CO_2 under metal-free system was reported by Fontaine and Maron et al. in 2013.[136] Phosphine−borane **21** (1 mol %) was employed for the reduction of CO_2 (1 atm) at room temperature in the presence of HBcat (eq 47). No adduct was formed when **21** was exposed to CO_2 (1 atm). Interestingly, other boranes, such as BH_3·SMe_2, BH_3·THF, 9-BBN, and HBpin also gave the products

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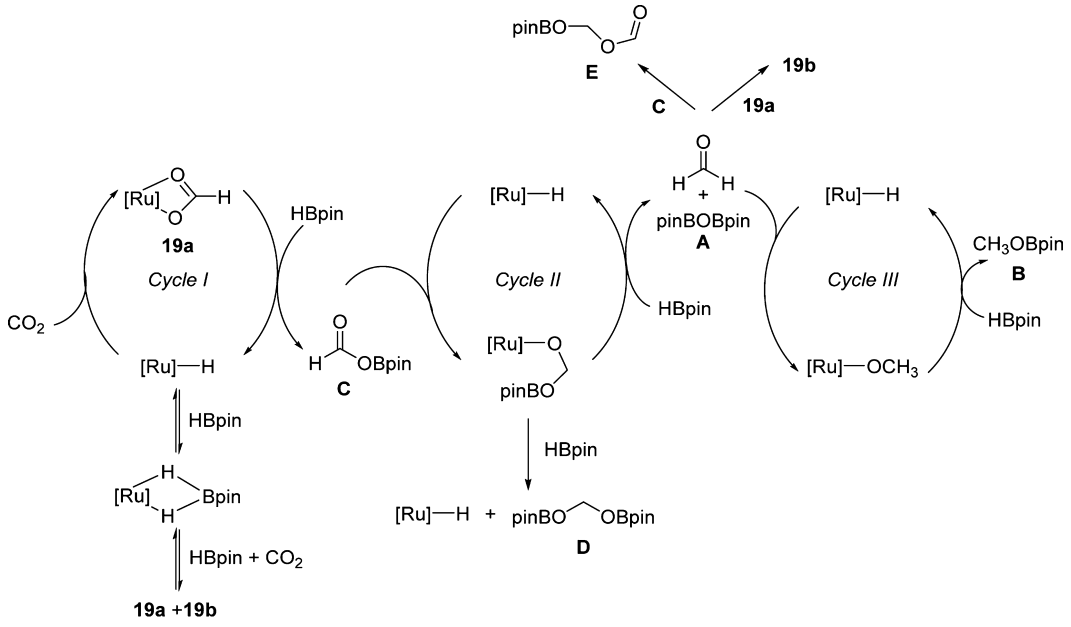
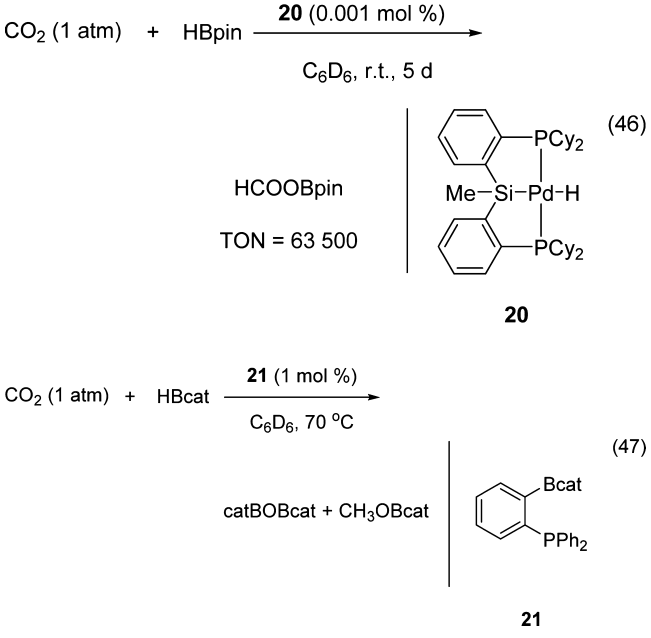
Scheme 20. Mechanism for Hydroboration of CO_2 Using 19

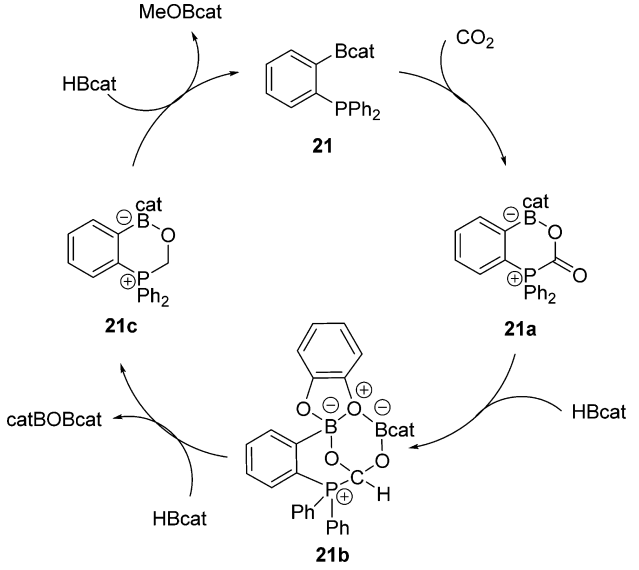




with reasonable TON and TOF values. The maximum TON (>2950) was achieved after 4 h by employing 1000 equiv of $BH_3{\cdot}SMe_2$ under CO_2 (2 atm) and heating at 70 °C.

On the basis of DFT calculation (B3PW91/6-31G** level of theory), the reaction mechanism was proposed (Scheme 21). First, **21** would activate CO_2 to form the adduct **21a**, which was found to be endothermic (ΔH = +9.9 kcal mol^{-1}). Addition of HBcat to this adduct yielded compound **21b** in a further favorable process (ΔH = −14.4 kcal mol^{-1}). Subsequent addition of HBcat would give hydroborated products and compounds **21c**, from which **21** would be regenerated. Although the authors attempted to synthesize **21b**, addition of 3 equiv of HBcat to **21a** in the absence of CO_2 afforded only CH_3OBcat (90% conversion) after 20 h at room temperature. Formaldehyde was postulated to exist in the solution, given that an unassigned peak in NMR analysis could be reproduced when reacting **21** with paraformaldehyde at 70 °C for 15 min.

Scheme 21. Proposed Mechanistic Cycle for Catalytic Hydroboration of CO_2 Using 21



In 2014, Stephan et al. described the synthesis of intramolecular FLPs **22a,b** by the ring expansion reaction of carbene-9-BBN adducts and employed them in catalytic hydroboration of CO_2.[137] Unlike a typical FLPs system, **22a,b** can be seen as a combination of a strong Lewis basic phosphorus site with a weak Lewis acidic borane site. In a typical example, a mixture of **22a** (5 mol %), CO_2 (5 atm), and HBpin (20 equiv) in C_6D_5Br at 60 °C produced hydroborated products (HCOOBpin, $pinBOCH_2OBpin$, and MeOBpin) in 95% yield (eq 48). The distribution of the hydroborated products depended on the concentration of HBpin. The use of HBcat or BH_3 instead of HBpin resulted in exclusive formation of MeOBcat and oxoborane $(MeOBO)_3$, respectively. They observed a higher reactivity of **22b** compared with **22a**, which is presumably due to the stronger Lewis basicity of the $P(N^iPr_2)_2$ site. A proposed mechanism includes an initial CO_2 activation,

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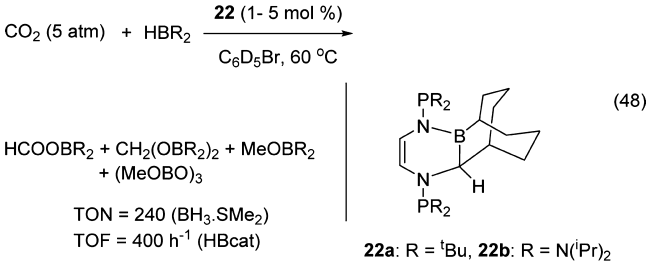
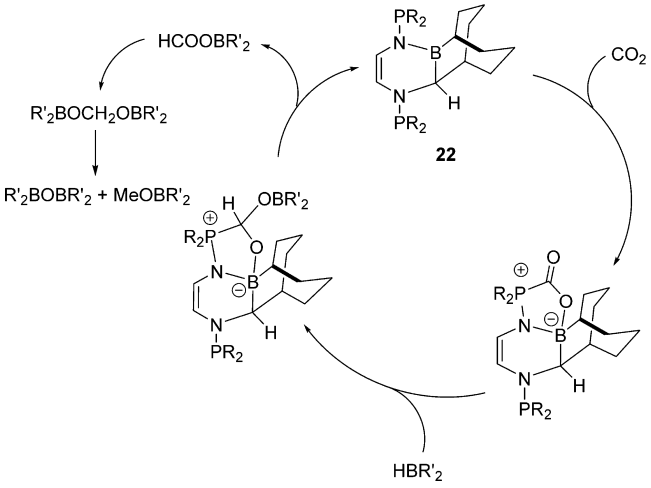


(48)

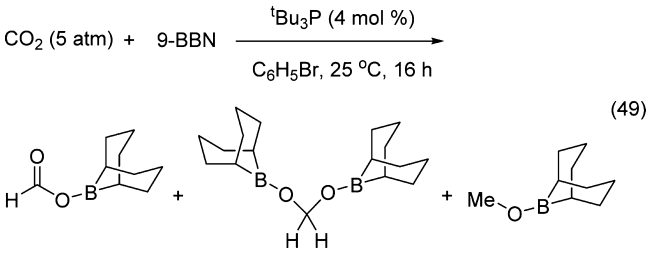
followed by reduction of C═O of formate moiety by HBR_2 in the second step. The final step would comprise the regeneration of catalyst with the formation of hydroborated products (Scheme 22).

Scheme 22. CO_2 Hydroboration Using Intramolecular FLP 22

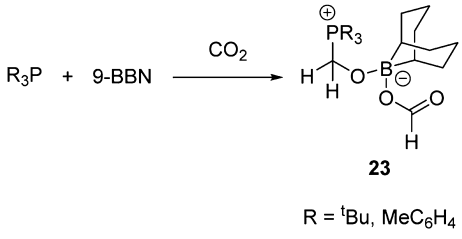


Stephan et al. also reported an intermolecular phosphine−borane system for reduction of CO_2.[138] A catalytic amount of $^tBu_3P$ (4 mol %) promoted reduction of CO_2 (5 atm) in the presence of 9-BBN (0.094 mmol) which rendered products HCOOBBN (36%), $NBBOCH_2OBBN$ (15%), and MeOBBN (49%) (eq 49). Lowering the catalyst loading from 4 mol % to 0.02 mol % increased the production of MeOBBN (98%). Other phosphines, such as Ph_3P, $(4\text{-}MeC_6H_4)_3P$, and $(3,5\text{-}Me_2C_6H_3)_3P$, also exhibited reasonable catalytic activity. Interestingly, an induction period was observed for arylphosphines; thus, an equilibrium could exist between the phosphine CO_2, and its adduct. From stoichiometric reactions of R_3P and 9-BBN, compound **23** was isolated and structurally characterized by X-ray analysis (eq 50). Addition of 9-BBN to **23** gave similar hydroborated products, suggesting the existence of **23** in the catalytic cycle (Scheme 23).

More recent examples have demonstrated that inexpensive alkaline earth metal complexes **24** are effective for the reduction of CO_2, as reported by Hill et al. (eq 51).[139] The reactions were performed at 60 °C and required 4−6 days for full conversion of HBpin. Importantly, the reduction of CO_2 produced CH_3OBpin as the major product, and a small (<5%) amount of HCOOBpin and $pinBOCH_2OBpin$ were observed. Stoichiometric addition of CO_2 to **24** gave a fascinating compound, **24a**, containing two bridging formate groups (eq 52). Complex **24a** also displayed reasonable catalytic performance under similar conditions. The role of **24a** in the reduction process is still unclear. Nonetheless, a plausible mechanism that involves several pathways was proposed (Scheme 24).

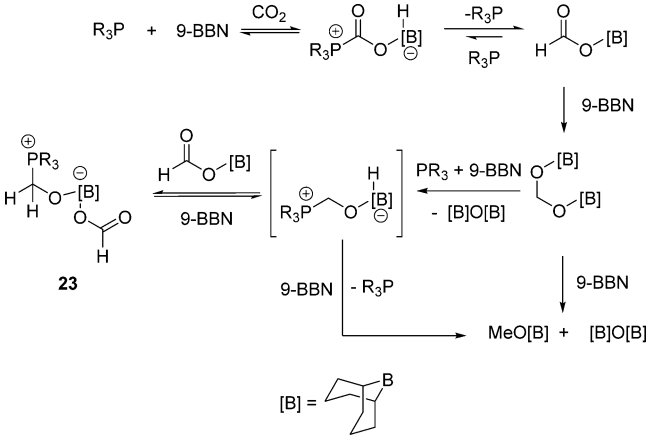


(49)



(50)

Scheme 23. Intermolecular R_3P-9-BBN System for Catalytic Hydroboration of CO_2



Analogous to the phosphine−borane system employed by Stephan, Cantat et al. employed nitrogen bases **25**−**28** as catalysts for CO_2 reduction to methanol (Figure 8).[140] A maximum TON of 648 and TOF of 33 h^{-1} were achieved with **26** (0.1 mol %) and 9-BBN under CO_2 (1 atm) at 25 °C after 20 h (eq 53). The initial hydroborated product was formate species HCOOBBN, which was rapidly converted to $H_2C(OBBN)_2$, and finally, MeOBBN was formed. The rate of the catalytic reaction depends on the borane reagent as well as the type of nitrogen base used. For instance, no catalytic reaction was observed using a combination of **27** and HBcat.

The reaction mechanism was investigated thoroughly by stoichiometric reactions and DFT studies. Interestingly, it was found that **25** and **26** catalyzed the reaction via two different pathways. Compound **25** activated CO_2 by increasing the nucleophilicity of O but maintaining the electrophilicity of C, whereas **26** increased the hydridic character of B−H bond in 9-BBN. Both mechanisms are summarized in Scheme 25.

Previous examples demonstrated the reduction of CO_2 to afford a C_1-bulding block, such as methanol, formaldehyde, and formic acid. In particular, formaldehyde and formic acid could react with amines to produce imines separately as aforementioned in the system reported by Nozaki and Sabo-Etienne

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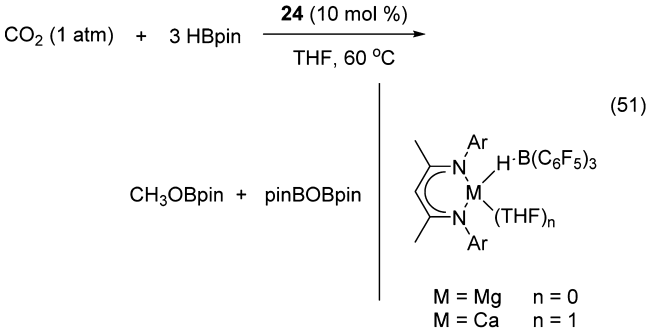
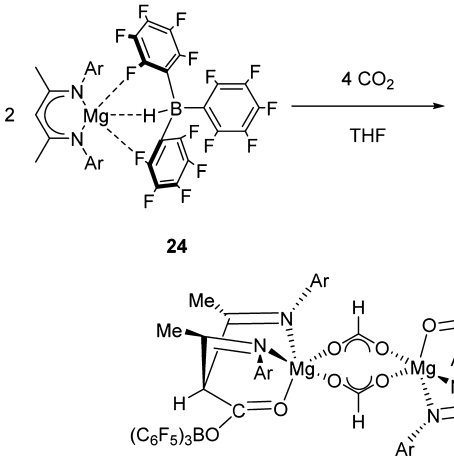


(51)

24

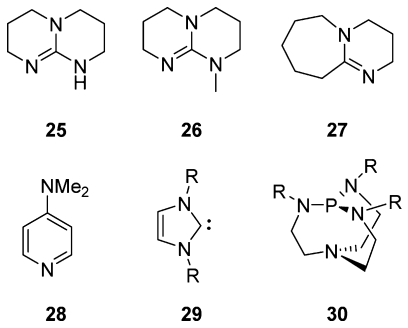


24

(52)

24a

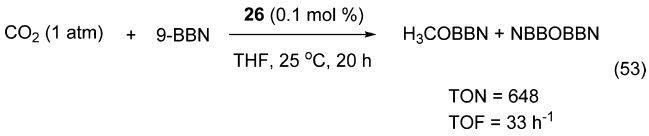
et al. Recently, Cantat et al. demonstrated several metal-free molecules, such as nitrogen bases (**25**−**28**), NHCs (**29**), and proazaphosphatranes (**30**), were effective as catalysts for hydroboration of CO_2 to methylamines.[141] The most efficient condition employed **30** (1.0 mol %), 9-BBN (0. 80 mmol), CO_2 (1 atm), and diphenylamine (0.20 mmol) at 90 °C in



25 **26** **27**

28 **29** **30**

Figure 8. Catalysts employed by Cantat and co-workers in their reduction of CO_2.



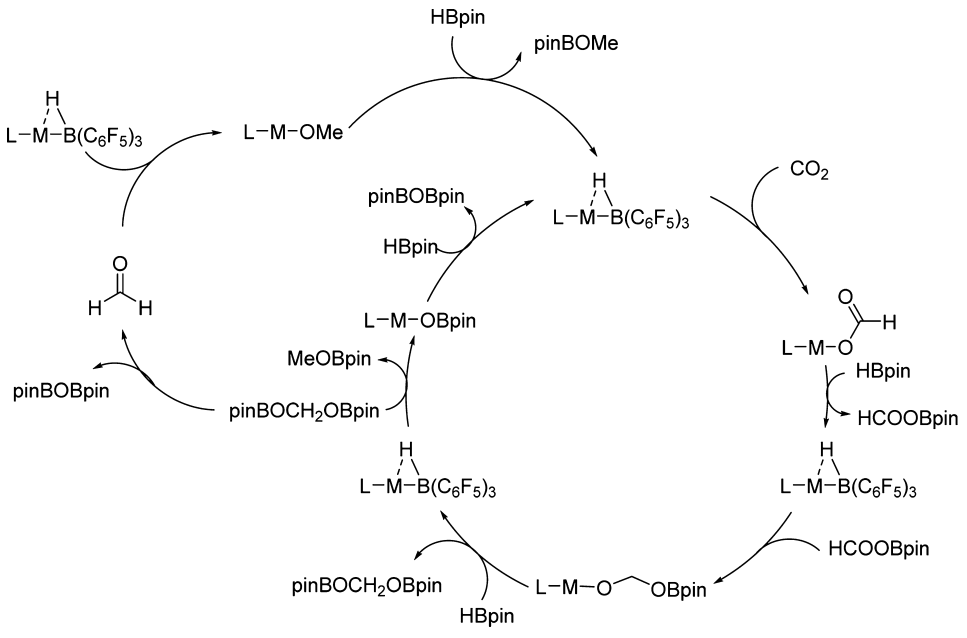
(53)

THF (eq 54). Impressively, this is the first demonstration of metal-free methylation of amines using CO_2. Notably, the use of other borane reagents, such as HBcat, HBpin, and BH_3·SMe_2 did not provide any methylated amines. Both the temperature and solvent affect the yields. Various secondary amine substrates, including electron-withdrawing, electron-donating groups, and also bulky substrates, were well tolerated.

Significantly, in the presence of additional equivalents of 9-BBN under the same reaction conditions, primary amines were converted to dimethylated product (eq 55). Moreover, conducting the catalytic reaction with an amine containing a ketone substituent gave a mixture of products, including a deoxygenated product (eq 56). The catalytic system was also versatile in reducing nitroarenes to the corresponding dimethylamines (eq 57).

In a mechanism investigation, Cantat et al. found that **30** could efficiently catalyze the hydroboration of CO_2 to give CH_3OBBN, with maximum TON of 6043. However, reaction

Scheme 24. Proposed Mechanism for Catalytic Reduction of CO_2 by Alkaline Earth Metal Complex 24



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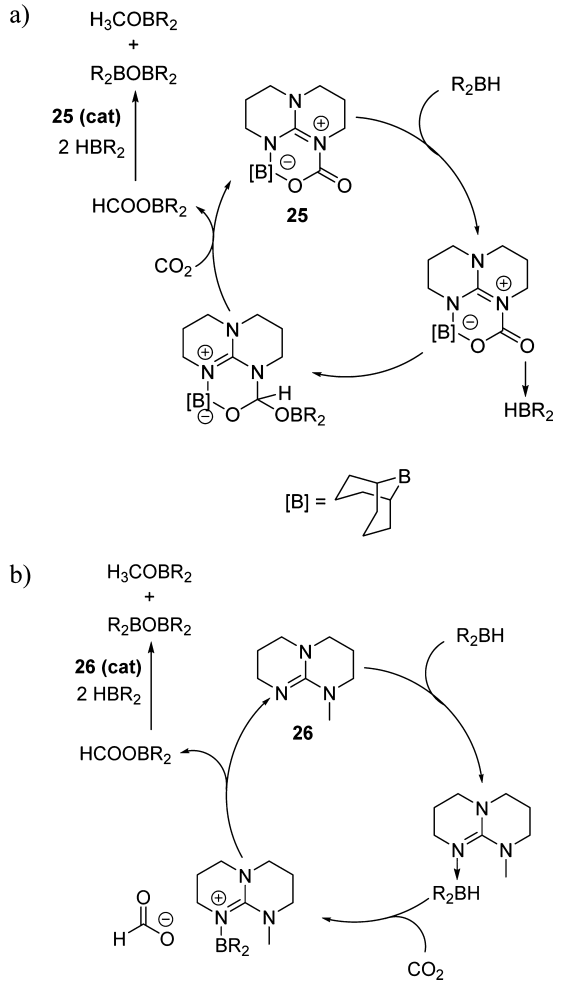
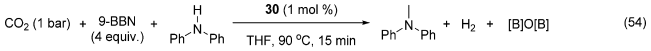
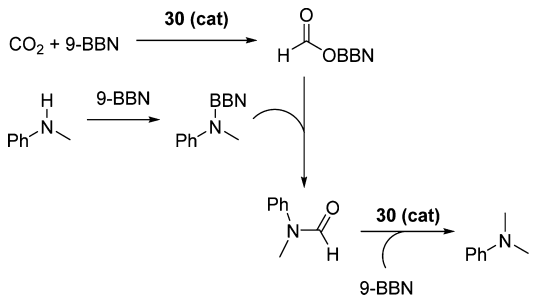
Scheme 25. Proposed Mechanism for (a) CO_2 Activation by 25 and (b) B−H Activation by 26





of CH_3OBBN with *N*-methylaniline did not afford the corresponding methylamine, even in the presence of **30** and 9-BBN. Importantly, they observed that reaction of *N*-methylaniline with 9-BBN produced the corresponding *N*-borylamines when heated at 100 °C for 1 h. Further reaction of *N*-borylamine with 9-BBN in the presence of **30** (1 mol %) gave the *N*-methylated amine (eq 58). Formation of formamide was postulated in the reaction, and the proposed mechanism is summarized in Scheme 26.

Scheme 26. Proposed Mechanism for Catalytic Reduction of CO_2 to Methylamine with 30



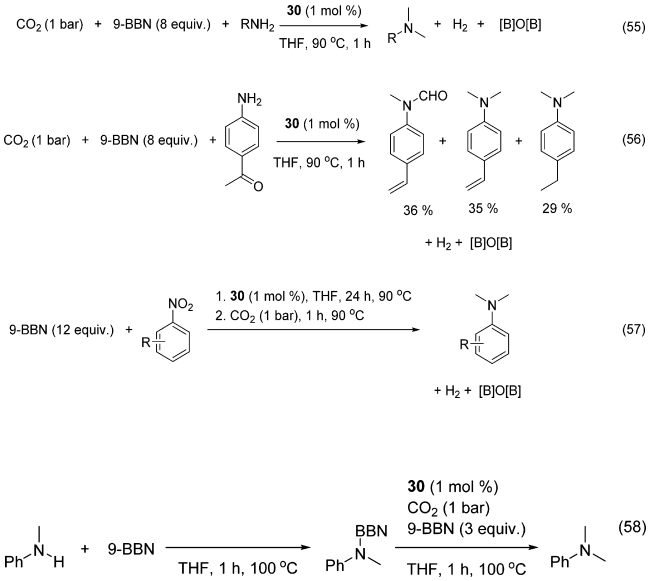


Table 1 summarizes the catalytic performances for hydroboration of CO_2 with various catalysts. HBpin and HBcat are commonly utilized in both transition metal catalysis and main group catalysis, and 9-BBN is mainly employed in main group catalysis. Remarkably, most catalytic reactions can be conducted under 1 atm and ambient conditions. Among transition metal catalysts, Ni complex **16** and Pd complex **20** display a high TOF (495, >8500, respectively). In main group catalysts, intramolecular FLP systems **21**, **22** and proazaphosphatranes **30** show a relatively high catalytic activity under heating conditions. The hydroboration products vary according to the reaction conditions, and thus, both transition metal catalysis and main group catalysis must be useful depending on the reaction target molecules.

8. CONCLUSION

In summary, we have intensively reviewed recent advances in catalytic hydroboration reaction of carbonyl compounds, imine derivatives, and carbon dioxide. Not only transition metals but also main group compounds exhibit efficient catalytic ability in the reaction. Theoretical studies could also support experimental data in comprehending details of the reaction mechanism. For hydroboration of carbonyl and imine derivatives, reaction mechanism with metal catalysts involves several pathways, whereas main-group-catalyzed hydroboration proceeds via a relatively simple process, such as σ-bond metathesis or a zwitterionic mechanism. Meanwhile, for hydroboration of CO_2, most reactions involve activation of CO_2 as an initial step prior to generating products. The potential of hydroboration reactions is not limited to addition of H−B bonds across unsaturated bonds. For instance, reduction of CO_2 affords a variety of compounds, including formaldehyde and formic acid equivalents, that could be transformed in one pot to methylated amines by further reaction with primary and secondary amines under catalytic conditions. Hence, the numerous plausible applications of hydroboration reaction in synthetic chemistry can be expected. Future work, in particular using main group catalysts, will involve reactions such as hydroboration of other unsaturated bonds rarely explored thus far and the development of various one-pot reduction−transformation sequences, as well as their application in asymmetric synthesis.

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Table 1. Overview of the Various Catalytic Performances for Hydroboration of CO_2

	catalyst	catalyst loading (mol %)	borane	reaction conditions	products	TOF (h^{-1})
transition metal catalysts	**15**	10	HBpin	1 atm CO_2, THF, 35 °C, 24 h	HCOOH	0.4
	16	0.2	HBcat	1 atm CO_2, C_6D_6, r.t., 1 h	MeOBcat, $O(Bcat)_2$	**495**
	17	1	HBpin	1 atm CO_2, CD_2Cl_2, 50 °C, 96 h	MeOBpin, $O(Bpin)_2$	0.1
	18	10	HBpin	1 atm CO_2, C_6D_6, r.t., 0.5 h	HCOOBpin, MeOBpin, $CH_2(OBpin)_2$, $HCOOCH_2OBpin$, $O(Bpin)_2$	20
	19	10	HBpin	1 atm CO_2, C_6D_6, r.t., 0.5 h	CH_2O, MeOBpin, $CH_2(OBpin)_2$, $HCOOCH_2OBpin$, $O(Bpin)_2$	20
	20	0.01	HBpin	1 atm CO_2, C_6D_6, r.t., <1 h	HCOOBpin	**>8500**
main-group catalysts	**21**	0.3	BH_3SMe_2	2 atm CO_2, C_6D_6, 70 °C, 1 h	MeOBcat, $O(Bcat)_2$	**853**
	22	1	HBcat	5 atm CO_2, C_6D_5Br, 60 °C, 0.25 h	MeOBcat	**400**
	$P(^tBu)_3$	0.02	9-BBN	5 atm CO_2, C_6H_5Br, 60 °C, 32 h	HCOO[B], MeO[B], $[OB]_2CH_2$	170
	24	10	HBpin	1 atm CO_2, THF, 60 °C, 6 d (M = Mg), 4 d (M = Ca)	MeOBpin, $O(Bpin)_2$	0.069 (M = Mg) 0.1 (M = Ca)
	25	0.1	9-BBN	1 atm CO_2, THF, r.t. 147 h	MeO[B], $[B]_2O$	3.6
	26	0.1	9-BBN	1 atm CO_2, THF, r.t. 20 h	MeO[B], $[B]_2O$	33
	30	1	9-BBN	1 atm CO_2, Ph_2NH, THF, 90 °C, 0.25 h	Ph_2NMe, H_2, $[B]_2O$	**364** (R = Me) **372** (R = ^{i}Pr)

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Notes

The authors declare no competing financial interest.

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