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Hydrosilylation of Carbonyls Catalyzed by Hydridoborenium Borate Salts: Lewis Acid Activation and Anion Mediated Pathways

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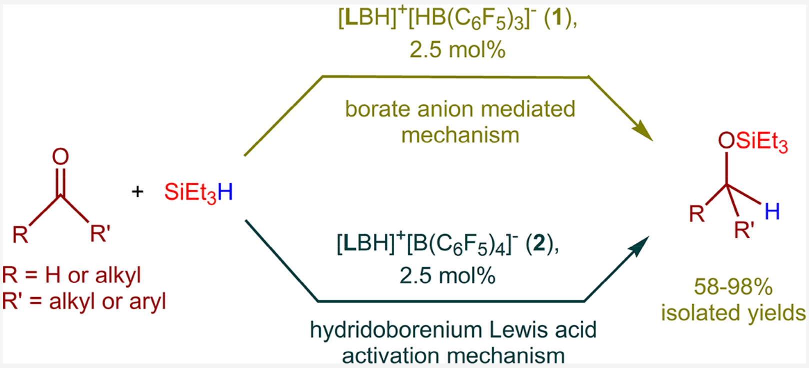

ABSTRACT: The electronically unsaturated three-coordinated hydridoborenium cations $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) and $[LBH]^+[B(C_6F_5)_4]^-$ (**2**), supported by a bis(phosphinimino)amide ligand, were found to be excellent catalysts for hydrosilylation of a range of aliphatic and aromatic aldehydes and ketones under mild reaction conditions (**L** = $[\{(2,4,6\text{-}Me_3C_6H_2N)P(Ph_2)\}_2N]$). The key steps of the catalytic cycle for hydrosilylation of PhCHO were monitored via in situ multinuclear NMR measurements for catalysts **1** and **2**. The combined effect of carbonyl activation via the Lewis acidic hydridoborenium cation and the hydridic nature of the borate counteranion in **1** makes it a more efficient catalyst in comparison to that of carbonyl activation via the predominant Lewis acid activation pathway operating with catalyst **2**. The catalytic cycle of **1** showed hydride transfer from the borate moiety $[HB(C_6F_5)_3]^-$ to PhCHO in the first step, forming $[PhCH_2{-}O{-}B(C_6F_5)_3]^-$, which subsequently underwent σ-bond metathesis with Et_3SiH to form the product, $PhCH_2{-}O{-}SiEt_3$. Quantum chemical calculations also support the borate anion mediated mechanism with **1**. In contrast, the reaction catalyzed by **2** proceeds predominantly via the Lewis acid activation of the carbonyl group involving $[LB(H){\leftarrow}OC(H)Ph]^+[B(C_6F_5)_4]^-$ as the transition state and $[LBOCH_2Ph]^+[B(C_6F_5)_4]^-$ as the intermediate.

INTRODUCTION

Over the past decades, the hydrosilylation of >C=X (O, CR_2, NR) functional groups has become a viable alternative to other commonly known reduction protocols such as hydrogenation using molecular hydrogen, use of hydride donor agents, and transfer hydrogenation.[1] For the direct synthesis of silyl ethers (or protected alcohols), the hydrosilylation of carbonyls mediated by precious-transition-metal catalysts (Pd, Pt, Rh, Ir, etc.) is a convenient route.[2] The rapidly growing interest in the catalytic application of inexpensive, eco-friendly, and less toxic metal complexes such as those of Fe, Co, Mn, Cu, and Ni in the activation of Si−H bonds has also been witnessed recently.[3] However, there has been limited success in matching the activity of precious-metal complexes with that of catalysts based on late transition metals. More recently, complexes from main-group elements have started to emerge as hydroelementation catalysts and as alternatives to both the precious-metal as well as the late-3d-metal complexes and are expected to show rapid future growth.[4]

Toward the goal to develop non-transition-metal-based catalysts, in the late 90s Piers and co-workers used $B(C_6F_5)_3$ as a catalyst for hydrosilylation of carbonyl compounds, including esters and olefins.[4,5] This work marked a major step toward the application of main-group complexes as catalysts. Subsequently, the groups of Harder, Manners, Dagorne, Inoue, Nikonov, Roesky, Singh, Hill, Ingleson, and a few others have made individual notable contributions in the development of main-group catalysts such as applications of the complexes of Mg,[6] Ca,[7] B,[8] Al,[9] Si,[10] P,[11] etc. in various organic transformations. Additionally, Okuda and co-workers reported on the chemoselective hydroboration of carbonyl compounds

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with lighter alkali-metal hydridoborates, $[(L)M][HBPh_3]$ (M = Li, Na, K; L = tris{2-(dimethylamino)ethyl}amine).[12] Interestingly, among these boron remained as one of the most attractive targets to explore the catalytic role of its complexes for hydroelementation reactions.[8,12,13] Boron compounds capable of exhibiting strong Lewis acidic behavior, such as $B(C_6F_5)_3$, were very promising candidates.[13] In this context, cationic complexes of boron were supposed to fulfill the requirements of Lewis acidity even better.[14,15] It has been shown that borenium cations offer a perfect balance of stability and Lewis acidity.[16,17]

Borenium cations with a hydride functionality have been considered important reagents with potential applications as metal-free catalysts in processes such as hydrogenation,[18a,b] imine hydrogenation,[18c] dihydrogen activation, and alkyne 1,2-carboboration.[19] At present, a few well-characterized cationic mononuclear borenium hydride species are known.[20−24] Previously, we have synthesized the borenium hydride cations $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) and $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) (Figure 1) supported by a bis(phosphinimino)amide ligand and demonstrated their Lewis acid behavior as well.[22,24] In a continuation of our efforts to exploit the Lewis acidity of these ionic complexes and to discover new catalysts from main-group compounds, herein we employed **1** and **2** for the hydrosilylation of aldehydes and ketones (Figure 1). Currently, only two reports are available that utilize $[\text{9-BBN}\cdot(\text{2,6-lutidine})]^+NTf_2^-$ and $\{Al[OC(CF_3)_3]_4\}^-$ salts of a ferrocene-based planar-chiral borenium cation to catalyze the hydrosilylation of ketones.[14a,d] Mechanistic investigations of these catalysts suggest the borenium ion activation of Et_3SiH as the key step, similar to that outlined for $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyls by Piers and co-workers.[4c] In contrast to these, herein we have observed that the hydride functionality plays an important role in catalysts **1** and **2** and that these catalysts adopt reaction pathways different from those for previously reported borenium ion catalyzed carbonyl hydrosilylations. The combination of the Lewis acidic hydridoborenium cation and the hydridic borate in **1** assist the catalysis reaction more efficiently in comparison to the predominant Lewis acid activation mechanism operating with catalyst **2**. Additionally, the intermediate $[LBH]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ (S_1**2**), formed from the reaction between **1** and PhCHO, was a key intermediate that was successfully isolated and characterized. This intermediate was further used as a precatalyst for hydrosilylation of another carbonyl substrate to experimentally support the hydride migration from the hydridic borate to the carbonyl as the key step of the hydrosilylation involving **1**.

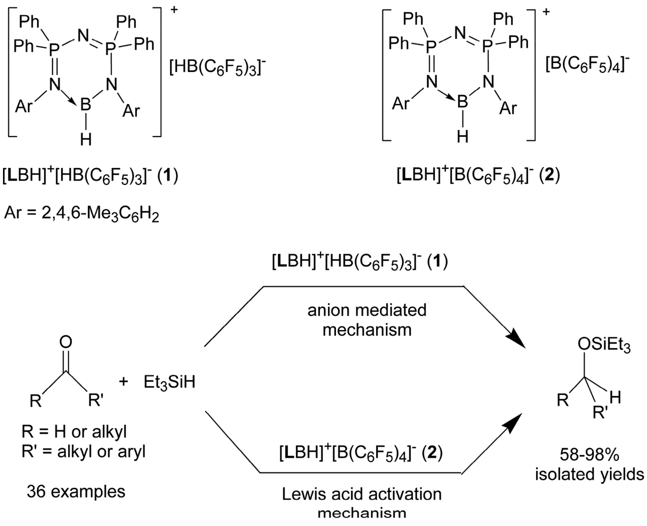


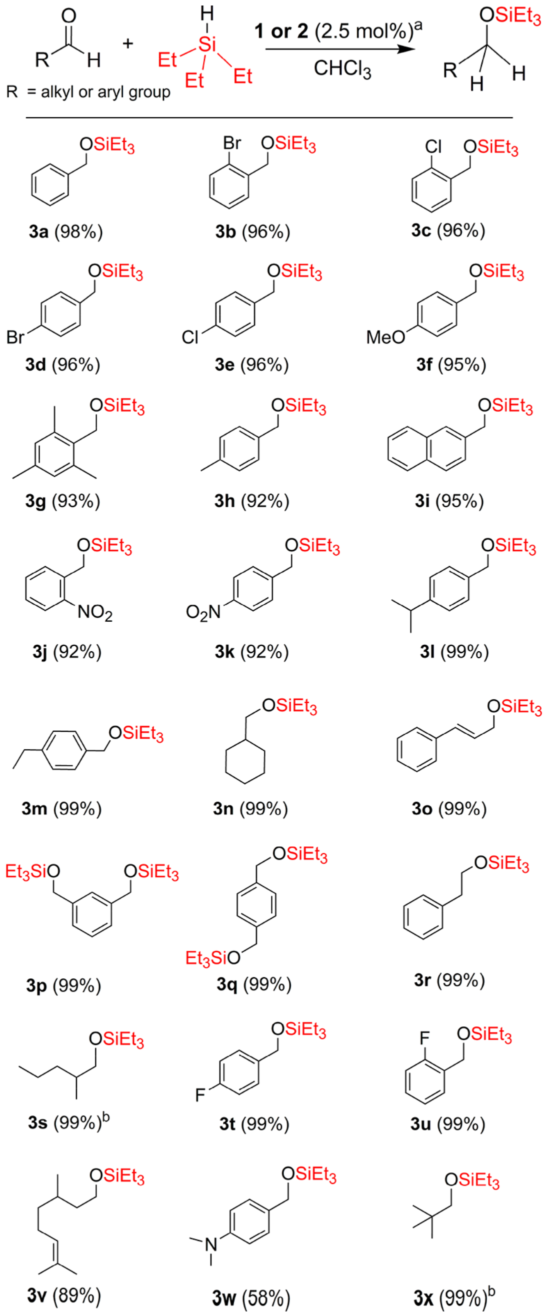
Figure 1. (top) Hydridoborenium cations (**1** and **2**). (bottom) Hydrosilylation of carbonyl compounds. Hydrosilylation catalyzed by **1** involves $[HB(C_6F_5)_3]^-$ as the hydride source, whereas with **2** the reaction proceeds with Lewis acid activation of the carbonyl group.

RESULTS AND DISCUSSION

The hydridoborenium borate ion pairs $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) and $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) were generated by hydride abstraction from LBH_2 with $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$, respectively (LH = $[\{(2,4,6\text{-}Me_3C_6H_2N)P(Ph_2)\}_2N]H$).[24] Compounds **1** and **2** proved to be efficient catalysts for the hydrosilylation of carbonyl compounds (aliphatic and aromatic aldehydes and ketones) in $CHCl_3$ medium and showed good catalytic activity at 40 and 70 °C, respectively. In a control experiment, under similar catalytic reaction conditions, the use of LBH_2 as the catalyst showed no reaction between benzaldehyde and Et_3SiH. This study justified the need for generation of the cationic complexes **1** and **2** from their common precursor, LBH_2. The reaction conditions for hydrosilylation (with respect to the relative quantity of reagents and catalyst, reaction temperature, and duration) were optimized by using benzaldehyde as the benchmark substrate (see the Supporting Information). Reducing the catalyst loading from 5 mol % to 2.5 mol % does not affect the conversion of the desired product; however, a catalyst loading lower than 2.5 mol % increased the reaction duration, slowed the conversion, and lowered the purity of the product. Good catalyst performance was thus obtained on employing 2.5 mol % of **1** or **2** and 1.0 mmol of benzaldehyde with 1.2 mmol of Et_3SiH in $CHCl_3$. Under these conditions, quantitative conversion of benzaldehyde to $Et_3Si{-}O{-}CH_2Ph$ (**3a**) occurred after 1 h at 40 °C with catalyst **1** and after 7 h at 70 °C with catalyst **2**. Usually, solvents play an important role, possibly by interacting with the transient or stable species formed during the course of the catalytic reaction.[25] Chloroform was found to be the most suitable solvent among the solvents compatible with this reaction (toluene, THF, dichloromethane, and chloroform) (Tables S1 and S2 in the Supporting Information). Use of a polar coordinating solvent such as THF slowed down the reaction, probably due to the formation of the coordinatively saturated THF adduct of **1** and **2** that delays the substrate binding to the boron center. The formation of **3a** was confirmed by its ^1H NMR spectrum, which showed a singlet corresponding to the benzylic $-CH_2$ moiety at 4.73 ppm. A quartet and triplet due to the $-OSiEt_3$ group appeared at 0.64 and 0.97 ppm, respectively. In the ^{13}C NMR spectrum, signals for $-OSiEt_3$ (4.5 and 6.8 ppm) and $-CH_2OSiEt_3$ (64.7 ppm) as a result of hydrosilylation also revealed the formation of **3a**. Subsequently, various aldehydes and ketones were smoothly converted to their corresponding silyl ethers **3a−x** (Table 1) and **4a−l** (Table 2), respectively, in very good yields under the optimized reaction conditions.

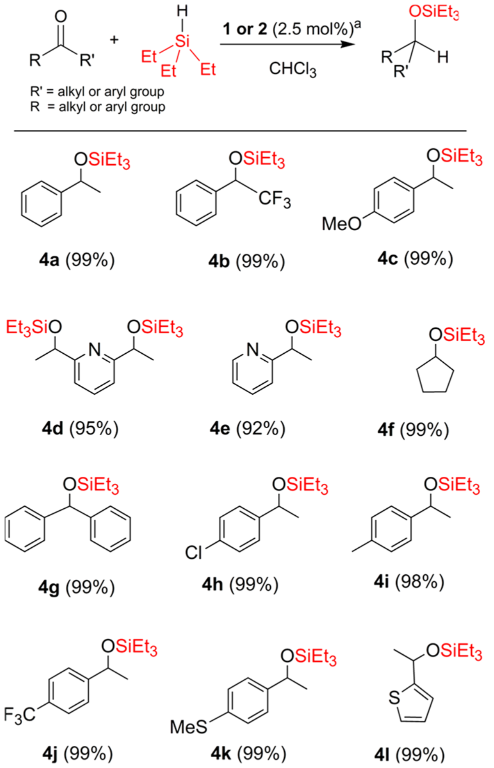
Halogenated benzaldehydes could be easily converted to their corresponding triethylsilyl ethers (**3b−e**,**t**,**u**), and no σ-bond metathesis between the halogen moiety and Et_3SiH was observed. In our attempts to explore the substrate scope, we have also been able to demonstrate good chemo- and regioselectivity of our catalysts toward carbonyls in the

Table 1. Substrate Scope of Hydrosilylation of Aldehydes Catalyzed by Hydridoborenium Borate Salts 1 and 2



[a]Values in parentheses indicate the yields of isolated products that were characterized by ^{1}H and ^{13}C NMR. Reactions were performed at 40 °C (for cat. **1**) and 70 °C (for cat. **2**). [b]Due to volatile nature of the product the yield was calculated by NMR using hexamethylbenzene as an internal standard.

Table 2. Substrate Scope of Hydrosilylation of Ketones Catalyzed by Hydridoborenium Borate Salts 1 and 2



[a]Values in parentheses indicate the yields of isolated products that were characterized by ^{1}H and ^{13}C NMR. Reactions were performed at 40 °C (for cat. **1**) and 70 °C (for cat. **2**).

presence of different functional groups such as conjugated or isolated olefins (**3o**,**v**), where only 1,2-addition took place and the double bond of the substrate remained intact. In the case of hydrosilylation of heteroaromatic ketones such as 2-acetylpyridine, 2,6-diacetylpyridine, and 2-acetylthiophene a good tolerance toward the dearomatization of the heteroaromatic rings[6b,7c,11d] was observed and smooth reduction of the ketone group took place to afford their corresponding silyl ethers **4d**,**e**,**l** (Table 2). Further, substrates containing two carbonyl groups in conjugation with the aromatic rings such as isophthalaldehyde, terephthalaldehyde, and 2,6-diacetylpyridine furnished the reduction of both carbonyl moieties, yielding **3p**,**q** and **4d**, respectively.

Mechanistic Investigations of Hydrosilylation of Carbonyl Compounds with $[LBH]^+[HB(C_6F_5)_3]^-$ (1) as the Catalyst. To elucidate the mechanism of reaction by the present catalysts, we first performed the stoichiometric reaction of $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) with PhCHO and monitored the progress of the reaction using hetronuclear NMR spectroscopy. These investigations clearly identified the intermediate $[LBH]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ (**S$_1$2**), formed as a result of hydride migration from $[HB(C_6F_5)_3]^-$ to PhCHO (Figure 2). Intermediate **S$_1$2** was stable enough to be isolated and characterized by using multinuclear NMR (^{1}H, ^{13}C{^{1}H}, ^{11}B, ^{31}P{^{1}H}, and ^{19}F) and IR spectroscopy. The disappearance of the aldehydic PhC*HO* peak in the ^{1}H NMR spectrum and absence of a carbonyl >C═O stretching frequency in the IR spectrum confirmed the formation of **S$_1$2**. The formation of **S$_1$2** was facile at room temperature, and subsequent addition of an stoichiometric amount of Et_3SiH gave the product **3a**. The formation of **3a** was slow at room temperature but can be expedited by heating the reaction mixture to 40 °C.

In the ^{1}H NMR spectrum of the reaction mixture, the appearance of a signal at 4.46 ppm was assigned to the benzylic $-CH_2$ moiety of $[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ (**S$_1$2**). Upon addition of Et_3SiH a downfield shift for $-CH_2$ protons (4.73 ppm) was observed, which indicates the formation of $Et_3Si{-}O{-}CH_2Ph$ (**3a**) (Figure 3). The concomitant regeneration of **1** was also clear from the disappearence of the ^{11}B NMR signal

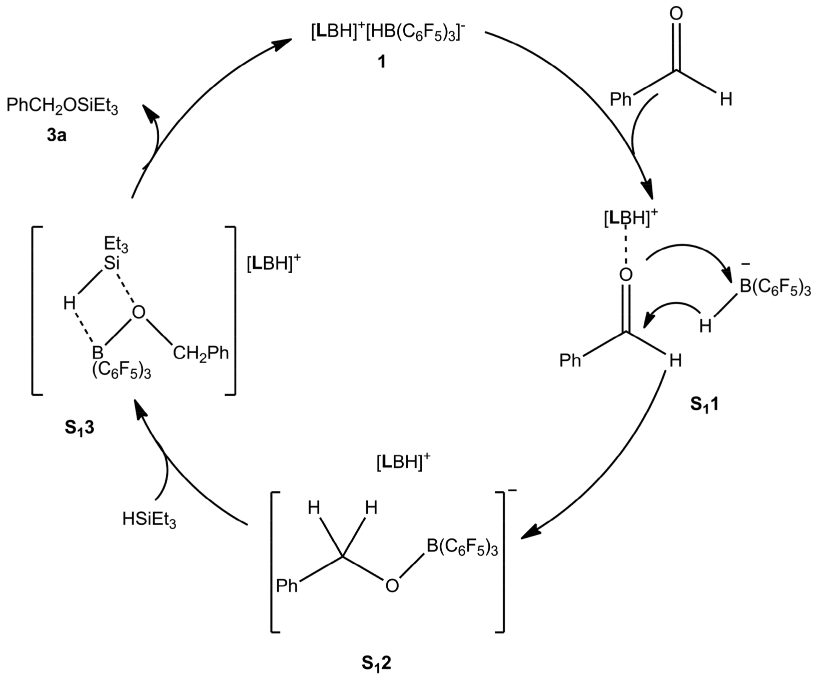


Figure 2. Proposed catalytic cycle for the hydrosilylation of PhCHO using Et_3SiH and the catalyst $[\mathbf{L}BH]^+[HB(C_6F_5)_3]^-$ (**1**).

at −2.50 ppm (for $[PhCH_2{-}O{-}\mathit{B}(C_6F_5)_3]^-$) and reappearance of the signal at −25.1 ppm (for $[HB(C_6F_5)_3]^-$). We propose that Et_3SiH reacts with $\mathbf{S_12}$ to form the four-membered cyclic transition state $\mathbf{S_13}$, which easily undergoes a σ-bond metathesis reaction at 40 °C to convert into **3a** and regenerate the catalyst **1**. Due to fast conversion of $\mathbf{S_13}$ into the product at 40 °C, we could not observe experimental evidence for $\mathbf{S_13}$, but computational studies suggest its involvement (see below Figure 4).

Recently, Vanka et al. performed computational work that supports the idea of $B(C_6F_5)_3$ to function more as an initiator rather than a pure catalyst in many metal-free transformations where the anion $[HB(C_6F_5)_3]^-$ is generated in the process and in further steps remains a spectator.[26] However, in the present work the anion $[HB(C_6F_5)_3]^-$ is not just a spectator but actually cooperatively participates in the reaction. Previously, Piers et al. also found hydride delivery from $[HB(C_6F_5)_3]^-$ in carbonyl hydrosilylation catalyzed by $B(C_6F_5)_3$.[4c] Similarly, insertion of CO_2 in the borohydride bond of $[HB(C_6F_5)_3]^-$ was observed by Ashley et al. when CO_2 was reacted with the salt $[Me_4C_5NH_2]^+[HB(C_6F_5)_3]^-$, leading to the formation of the structurally characterized formatoborate complex $[Me_4C_5NH]^+[HCO_2B(C_6F_5)_3]^-$.[27] Similarly, Parkin et al. reported the hydrosilylation of CO_2 by R_3SiH catalyzed with a combination of $\{[Tism^{iPrBenz}]M\}[HB(C_6F_5)_3]$ (M = Zn, Mg) and $B(C_6F_5)_3$. The CO_2 insertion into $[HB(C_6F_5)_3]^-$ was a crucial step of the reaction that formed the formatoborate-bridged complex $[Tism^{iPrBenz}]MOC(H)OB(C_6F_5)_3$, which was structurally characterized.[28] The zwitterionic phosphonium borate salt $(C_6H_2Me_3)_2P(H)CH_2CH_2B(H)(C_6F_5)_2$ reduces benzaldehyde stoichiometrically to give the benzyl alcohol derivative $(C_6H_2Me_3)_2P(H)CH_2CH_2B(OCH_2Ph)(C_6F_5)_2$.[29] Repo et al. demonstrated reduction of PhCHO using a stoichiometric amount of the borate $[Me_4C_5NH]^+[HB(C_6F_5)_3]^-$ and formation of $[Me_4C_5NH_2]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ as a result of PhCHO insertion into the B−H bond (where Me_4C_5NH = 2,2,6,6-tetramethylpiperidine).[30] Recently, in 2018, Mösch-Zanetti et al. showed the insertion of PhCHO into the B−H bond of the anion in $[Mo(OSiR_3)(NtBu)(2,4\text{-}tBu_2\text{-}6\text{-}\{(N\text{-}Ph)CH\}C_6H_2)]^+[HB(C_6F_5)_3]^-$, resulting in the formation of $[Mo(OSiR_3)(NtBu)(2,4\text{-}tBu_2\text{-}6\text{-}\{(N\text{-}Ph)CH\}C_6H_2)]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ (R = Et, Ph).[31] Given the fact that hydrosilylation with **1** involved the hydride transfer from the anion, we could not ascertain from our experiments the role of the cation in **1**; however, it is likely that the cation assists in activating the carbonyl in this process and facilitates the hydride transfer from the anion $[HB(C_6F_5)_3]^-$. Lewis acids such as $B(C_6F_5)_3$ are known to form weak labile adducts with carbonyl oxygen. Piers et al. found hydride abstraction from R_3SiH by $B(C_6F_5)_3$ via $[Et_3Si{-}{-}H{-}B(C_6F_5)_3]$ as the key activating step in $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyls.[4a,c] In view of this, we were prompted to see the involvement of such a species in the present case; therefore, when equimolar quantities of **1** and Et_3SiH were mixed, no evidence for the formation of $\mathbf{L}BH_2$ and $[Et_3Si{-}{-}H{-}B(C_6F_5)_3]$ or even $[\mathbf{L}(H)B{-}H{-}{-}{-}SiEt_3]^+[HB(C_6F_5)_3]^-$ was observed from ^1H, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra, which only showed signals for **1** and Et_3SiH. Thus, the alternative pathway involving borenium ion activation of Et_3SiH was not found to be convincing in this case (see Figure S19 in the Supporting Information).

To further verify our proposed mechanism, the isolated benzyloxyborate intermediate $[\mathbf{L}BH]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ ($\mathbf{S_12}$) was used in a separate reaction in a catalytic amount (5 mol %) for the hydrosilylation of isophthalaldehyde, which led to the formation of the product **3p** in quantitative yield. We anticipate that $\mathbf{S_12}$ first converted into equal amounts of **3a** and **1** and the re-formed catalyst **1** catalyzed the hydrosilylation of isophthalaldehyde (See Figures S8 and S9 in the Supporting Information). This reaction strengthens our claim of proposing $[\mathbf{L}BH]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ ($\mathbf{S_12}$) as the key intermediate.

Quantum Chemical Computational Results on the Catalytic Hydrosilylation of Benzaldehyde via an Anion

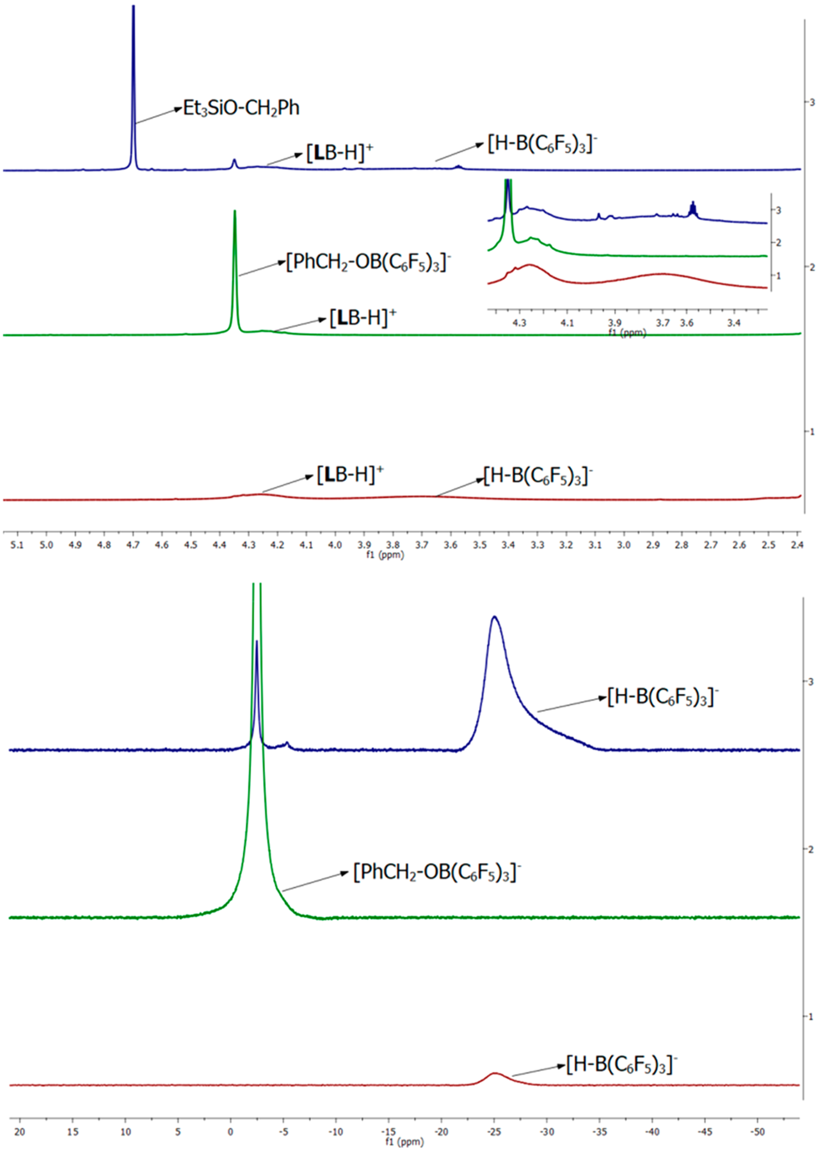


Figure 3. Stacked ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra of the stoichiometric reaction of $[\mathbf{L}\text{BH}]^+[\text{HB}(C_6F_5)_3]^-$ (**1**) with PhCHO in $CDCl_3$ to generate $\mathbf{S_12}$ and the subsequent reaction of $\mathbf{S_12}$ with Et_3SiH. The spectra in red are those of the catalyst $[\mathbf{L}\text{BH}]^+[\text{HB}(C_6F_5)_3]^-$ (**1**). The spectra in green show the characteristic signals of $\mathbf{S_12}$ (prepared in situ in a room-temperature reaction between **1** and PhCHO); note the appearance of the $-\text{OC}H_2\text{Ph}$ signal and disappearance of the signal for the anion $[H\text{B}(C_6F_5)_3]^-$. The spectra in blue show the formation of the product $Et_3Si-O-CH_2Ph$ (**3a**) upon addition of Et_3SiH at 40 °C and regeneration of **1**. The ^{11}B signal for the cationic B moiety was too broad to be observed due to low symmetry around the cationic B center in comparison to the anionic B center, which gives a sharp signal due to its higher symmetry and higher coordination number.

Mediated Pathway. The steps involved in the hydrosilylation of benzaldehyde with catalyst **1** were studied using computational methods. We have optimized the geometry and examined the changes in the electrostatic potential (ESP) of the possible intermediate steps and the final product and calculated their free energies in the solvent phase in ground states. The geometry optimizations, frequency calculations, and NBO analyses of all these structures have been carried out at the (U)M06-2X/CC-PVDZ level with CPCM as the solvent model and $CHCl_3$ as the solvent using the Gaussian09 suit of program.[32] The transition states were also investigated and confirmed by the IRC calculations employed in Gaussian09. The visualization of ESPs and MOs was done using Chemcraft[33] and Molden.[34]

Figure 4 depicts the energy profile diagram for the optimized intermediate species and the transition states involved. These computations reveal that $\mathbf{S_12'}$ (ΔG = −16.7 kcal/mol), corresponding to the anion of the experimentally observed intermediate $[\mathbf{L}\text{BH}]^+[PhCH_2-O-B(C_6F_5)_3]^-$ ($\mathbf{S_12}$), is thermodynamically stable and its formation takes place in spite of a large activation barrier ($\Delta G^\ddagger$ = 54.7 kcal/mol) via the transition state $\mathbf{S_11'}$. The formation of $\mathbf{S_12'}$ takes place via hydride transfer through a four-membered cyclic transition state with an imaginary frequency of −256.93 cm^{-1}. The transition state $\mathbf{S_11'}$ involves a weak interaction between PhCHO and $[\text{HB}(C_6F_5)_3]^-$, and the driving force for its conversion to $\mathbf{S_12'}$ could be due to the favorable interactions between an electrophilic carbonyl and a nucleophilic borate moiety (also favored by the electronegativity difference of B and O, 2.04 and 3.44, respectively, on the Pauling scale) as also depicted in the ESP plot of the complex between PhCHO and $[\text{HB}(C_6F_5)_3]^-$ (Figure S17 in the Supporting Information).

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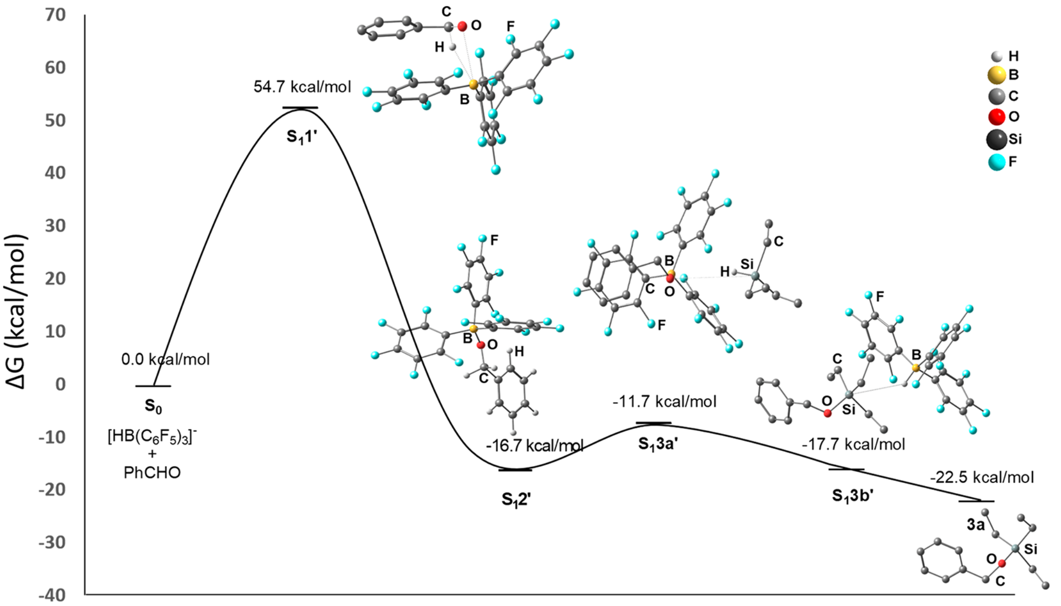

Figure 4. Free energy diagram for the hydrosilylation of benzaldehyde with Et_3SiH leading to the formation of $PhCH_2{-}O{-}SiEt_3$ via the anion $[HB(C_6F_5)_3]^-$ mediated pathway. The horizontal axis represents the arbitrary reaction coordinates.

The next step of the reaction involves the interaction of Et_3SiH with $\mathbf{S_12'}$ resulting in the formation of the product **3a** (−22.5 kcal/mol). We envisaged that formation of **3a** occurs via a cyclic transition state similar to that for $\mathbf{S_13}$ (Figure 2). However, our efforts to locate such a transition state were not successful. Instead, computationally we found that the transformation is favorable in two steps, which also seems to be consistent with our experimental observations. In this we allowed $\mathbf{S_12'}$ to interact with Et_3SiH, which afforded $\mathbf{S_13a'}$ (−11.7 kcal/mol) containing a weak Si- - -O interaction (3.73 Å) and elongated B−O bond (1.476 Å). Then $\mathbf{S_13a'}$ was allowed to rearrange into the slightly more stable species $\mathbf{S_13b'}$ (−17.7 kcal/mol). Species $\mathbf{S_13b'}$ basically consists of the complex $[PhCH_2{-}O{-}Et_3Si{-}{-}{-}H{-}{-}{-}B(C_6F_5)_3]^-$, which is even lower in energy than $\mathbf{S_13a'}$, with a weak interaction of hydride between boron and silicon. This complex easily releases the final product $PhCH_2OEt_3Si$ (**3a**) ($\Delta G = -22.5$ kcal/mol) and regenerates the borate anion $[HB(C_6F_5)_3]^-$. The combined outcome of $\mathbf{S_13a'}$ and $\mathbf{S_13b'}$ is reminiscent of the anticipated four-membered cyclic transition state $\mathbf{S_13'}$ involving σ-bond metathesis. Figure S17 in the Supporting Information shows the ESP plots of $\mathbf{S_12'}$, Et_3SiH, $\mathbf{S_13a'}$, and $\mathbf{S_13b'}$ supporting the interactions mentioned and the proposed transformations discussed above. Overall, this is consistent with the experimental observations that the anion plays the major role in catalyzing hydrosilylation of carbonyls with catalyst **1**.

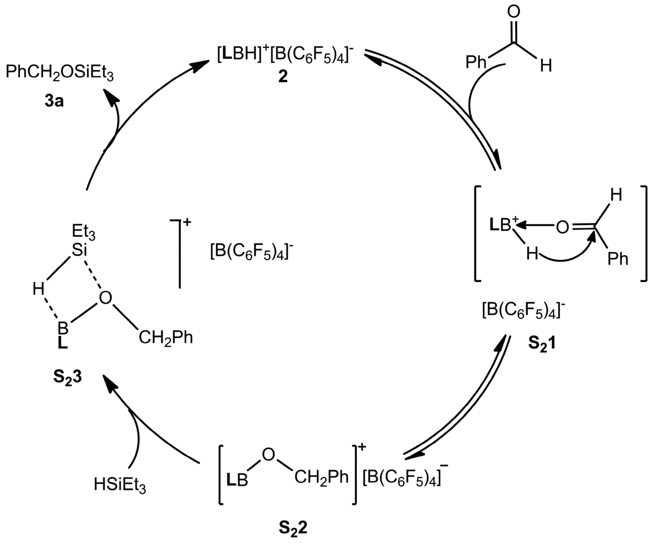

Figure 5. Proposed catalytic cycle for the hydrosilylation of PhCHO using Et_3SiH and the catalyst $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) via a Lewis acid mediated reaction pathway.

Mechanism of Hydrosilylation of Carbonyl Compounds with $[LBH]^+[B(C_6F_5)_4]^-$ (2) as the Catalyst. With clear spectroscopic evidence of involvement of the anion of $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) (Figure 3; *vide supra*) as the hydride source in the hydrosilylation of carbonyls with the cation possibly assisting in the Lewis acid activation of the >C=O group, it was worth investigating the same reaction using a similar hydridoborenium cation but with the counteranion devoid of any hydride. Therefore, the complex $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) was an ideal candidate for such investigations.[24] The stoichiometric reaction of $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) with PhCHO at 70 °C was followed by heteronuclear NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{11}B, ^{19}F, and ^{31}P{^{1}H}). Owing to the Lewis acidic nature of the cationic boron center of **2**, it can catalyze the reaction either via an aldehyde activation pathway or a silane activation[4c,14d] pathway. The NMR investigations of a mixture of **2** and PhCHO revealed a sluggish formation of the benzyloxy intermediate $[LB{-}O{-}CH_2Ph]^+[B(C_6F_5)_4]^-$ ($\mathbf{S_22}$) formed due to hydride transfer from $[LBH]^+$ to PhCHO along with unreacted **2** and PhCHO (Figure 5) probably forming an equilibrium. $\mathbf{S_22}$ was easily characterized by the characteristic $PhCH_2O$− signal at 4.44 ppm in the ^{1}H NMR spectrum of this mixture. It is proposed that the formation of $\mathbf{S_22}$ proceeds via the Lewis acid activation of the carbonyl group by the cationic boron hydride moiety (shown as $\mathbf{S_21}$) followed by hydride migration, a similar hydride migration to PhCHO was observed with a cationic aluminum hydride catalyst.[9a] It is possible that S_22 is labile with respect to its dissociation back into **2** and PhCHO (Figure 5). Addition of Et_3SiH to this mixture leads to a slow consumption of S_22, leading to the formation of the product **3a**. The possible pathway from S_22 to **3a** conversion could resemble a four-membered cyclic structure shown as S_23 that may involve σ-bond metathesis of Si−H and B−O bonds. The structure for S_23 is proposed in view of the absence of the involvement of silylium cation (see below) and also in view of a computed analogous transition state of our previous report on the hydroboration of carbonyls with a similar aluminum cation.[9a] The alternative silane activation pathway (see Figure S19 in the Supporting Information) was not supported by our observations from multinuclear NMR measurements, as the reaction between **2** and Et_3SiH did not provide evidence for the interaction of silane with the cationic boron center of **2**, thus eliminating the possibility of formation of species such as LBH_2 and silylium species $[Et_3Si]^+[B(C_6F_5)_4]^-$ or $[L(H)B{-}H{-}{-}{-}SiEt_3]^+[B(C_6F_5)_4]^-$. Additionally, the complete absence of deoxygenated product rules out the involvement of the silylium cation $[Et_3Si]^+[B(C_6F_5)_4]^-$ in the reactions catalyzed by **1** or **2**. This aspect has been thoroughly established by Piers and coworkers in their endeavor to establish the $[Et_3Si]^+[B(C_6F_5)_4]^-$-catalyzed mechanism of ketone hydrosilylation, where $PhCH_2CH_3$ and $Et_3SiOSiEt_3$ were the only products in $[Et_3Si]^+[B(C_6F_5)_4]^-$-catalyzed hydrosilylation of acetophenone using Et_3SiH as the hydride source.[4c]

CONCLUSIONS

In conclusion, the hydridoborenium salts $[LBH]^+[HB(C_6F_5)_3]^-$ (**1**) and $[LBH]^+[B(C_6F_5)_4]^-$ (**2**) were found to be good catalysts for the hydrosilylation of a variety of aldehydes and ketones in the presence of Et_3SiH. Catalysts **1** and **2** were easily obtained by hydride abstraction from LBH_2 using $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$, respectively ($L = [\{(2,4,6\text{-}Me_3C_6H_2N)P(Ph_2)\}_2N]$). On the basis of the observations from multinuclear NMR measurements it has been concluded that catalyst **1** involved the activation of the carbonyl group by hydride transfer from the borate anion $[HB(C_6F_5)_3]^-$ of **1** to the carbonyl carbon of benzaldehyde that formed a stable and isolable intermediate $[LBH]^+[PhCH_2{-}O{-}B(C_6F_5)_3]^-$ (S_12). The intermediate S_12 subsequently reacted with Et_3SiH via σ-bond metathesis of Si−H and B−O bonds to form the product $PhCH_2OSiEt_3$ and regeneration of the catalyst **1**. In contrast to **1**, the reaction mechanism for catalyst **2** was observed to proceed through the formation of a labile Lewis adduct between the hydridoborenium cation $[LBH]^+$ of **2** and the benzaldehyde oxygen. This adduct was thought to be responsible for the activation of benzaldehyde leading to the intermediate $[PhCH_2{-}O{-}BL]^+[B(C_6F_5)_4]^-$ (S_22), which is displaced into the product upon reaction with Et_3SiH at 70 °C. The reaction mechanism for catalyst **1** was also studied by a computational approach that supports our experimental observations for an anion-mediated pathway. Our experimental observations and outcome of the *in situ* NMR investigations revealed that the anion mediated pathway of catalyst **1** is more efficient than the Lewis acid mediated process of catalyst **2**. Currently, we are in the process of finding applications of these catalyst for other hydrofunctionalization reactions and carrying out a detailed investigation of their mechanisms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00646.

General information on synthetic methods, catalytic reactions, and characterization and computational analyses and tables (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Ojima, I. *The Hydrosilylation Reaction. Organic Silicon Compounds*; Wiley: Chichester, U.K., 1989. (b) Diez-Gonzalez, S.; Nolan, S. P. Copper, Silver, and Gold Complexes in Hydrosilylation Reactions. *Acc. Chem. Res.* **2008**, *41*, 349−358. (c) Marciniec, B. Catalysis by Transition Metal Complexes of Alkene Silylation-Recent Progress and Mechanistic Implications. *Coord. Chem. Rev.* **2005**, *249*, 2374−2390. (d) Troegel, D.; Stohrer, J. Recent Advances and Actual Challenges in Late Transition Metal Catalyzed Hydrosilylation of Olefins From an Industrial Point of View. *Coord. Chem. Rev.* **2011**, *255*, 1440−1459. (e) Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: Recent Advances and Perspectives. *RSC Adv.* **2015**, *5*, 20603−20616. (f) Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15−34. (g) Tahara, A.; Nagashima, H. Recent Topics of Iridium-Catalyzed Hydrosilylation of Tertiary Amides to Silylhemiaminals. *Tetrahedron Lett.* **2020**, *61*, 151423. (h) Khalimon, A. Y.; Gudun, K. A.; Hayrapetyan, D. Base Metal Catalysts for Deoxygenative Reduction of Amides to Amines. *Catalysts* **2019**, *9*, 490−516.

(2) (a) Tafazolian, H.; Yoxtheimer, R.; Thakuri, R. S.; Schmidt, J. A. Selective Hydrosilylation of Alkynes and Ketones: Contrasting Reactivity between Cationic 3-Iminophosphine Palladium and Nickel Complexes. *Dalton Trans.* **2017**, *46*, 5431−5440. (b) Kong, Y. K.; Kim, J.; Choi, S.; Choi, S. B. Hydrosilylation and Double Silylation of Carbonyl Compounds with 1,1′-Bis-(dimethylsilyl)ferrocene Using Nickel and Platinum-Catalysts. *Tetrahedron Lett.* **2007**, *48*, 2033−2036. (c) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. A Convenient and Novel Route to Bis(η-alkyne)platinum(0) and Other Platinum(0) Complexes from Speier's Hydrosilylation Catalyst $H_2[PtCl_6].xH_2O$. X-ray Structure of $[Pt\{(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}(P\text{-}t\text{-}Bu_3)]$. *Organometallics* **1987**, *6*, 191−192. (d) Zhao, L.; Nakatani, N.; Sunada, Y.; Nagashima, H.; Hasegawa, J. Y. Theoretical Study on the Rhodium-Catalyzed Hydrosilylation of C═C and C═O Double Bonds with Tertiary Silane. *J. Org. Chem.* **2019**, *84*, 8552−8561. (e) Park, S.; Brookhart, M. Hydrosilylation of Carbonyl-Containing Substrates Catalyzed by an Electrophilic η^1-Silane Iridium(III) Complex. *Organometallics* **2010**, *29*, 6057−6064.

(3) (a) Bleith, T.; Gade, L. H. Mechanism of the Iron(II)-Catalyzed Hydrosilylation of Ketones: Activation of Iron Carboxylate Precatalysts and Reaction Pathways of the Active Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 4972−4983. (b) Raya-Barón, A.; Oña-Burgos, P.; Fernández, I. Iron-Catalyzed Homogeneous Hydrosilylation of Ketones and Aldehydes: Advances and Mechanistic Perspective. *ACS Catal.* **2019**, *9*, 5400−5417. (c) Tamang, S. R.; Findlater, M. Emergence and Applications of Base Metals (Fe, Co, and Ni) in Hydroboration and Hydrosilylation. *Molecules* **2019**, *24*, 3194−4018. (d) Lipshutz, B. H.; Chrisman, W.; Noson, K. Hydrosilylation of Aldehydes and Ketones Catalyzed by $[Ph_3P(CuH)]_6$. *J. Organomet. Chem.* **2001**, *624*, 367−371. (e) Tran, B. L.; Pink, M.; Mindiola, D. J. Catalytic Hydrosilylation of the Carbonyl Functionality *via* a Transient Nickel Hydride Complex. *Organometallics* **2009**, *28*, 2234−2243. (f) Chakraborty, S.; Krause, J. A.; Guan, H. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes. *Organometallics* **2009**, *28*, 582−586. (g) Trovitch, R. J. The Emergance of Manganese-Based Carbonyl Hydrosilylation Catalysts. *Acc. Chem. Res.* **2017**, *50*, 2842−2852.

(4) (a) Parks, D. J.; Piers, W. E. Tris(pentafluorophenyl)boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters. *J. Am. Chem. Soc.* **1996**, *118*, 9440−9441. (b) Sakata, K.; Fujimoto, H. Quantum Chemical Study of $B(C_6F_5)_3$ Catalyzed Hydrosilylation of Carbonyl Group. *J. Org. Chem.* **2013**, *78*, 12505−12512. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. Studies on the Mechanism of $B(C_6F_5)_3$ Catalyzed Hydrosilation of Carbonyl Functions. *J. Org. Chem.* **2000**, *65*, 3090−3098. (d) Hog, D. T.; Oestreich, M. $B(C_6F_5)_3$ Catalyzed Reduction of Ketones and Imines Using Silicon-Stereogenic Silanes: Stereoinduction by Single-Point Binding. *Eur. J. Org. Chem.* **2009**, 5047−5056. (e) Rendler, S.; Oestreich, M. Conclusive Evidence for an S_N2-Si Mechanism in the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the Related Hydrogenation. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997−6000.

(5) Süsse, L.; Hermeke, J.; Oestreich, M. The Asymmetric Piers Hydrosilylation. *J. Am. Chem. Soc.* **2016**, *138*, 6940−6943.

(6) (a) Arrowsmith, M. Magnesium and Calcium Complexes in Homogeneous Catalysis. *Encyclopedia of Inorganic and Bioinorganic Chemistry.* **2015**, 1−26. (b) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C. Magnesium-Catalyzed Hydroboration of Pyridines. *Organometallics* **2011**, *30*, 5556−5559. (c) Weetman, C.; Hill, M. S.; Mahon, M. F. Magnesium-catalysed Hydroboration of Pyridines: Kinetic Analysis and Poly-pyridine Dearomatisation. *Polyhedron* **2016**, *103*, 115−120.

(7) (a) Harder, S. From Limestone to Catalysis: Application of Calcium Compounds as Homogeneous Catalysts. *Chem. Rev.* **2010**, *110*, 3852−3876. (b) Hill, M. S.; Liptrota, D. J.; Weetmana, C. Alkaline Earths as Main Group Reagents in Molecular Catalysis. *Chem. Soc. Rev.* **2016**, *45*, 972−988. (c) Intemann, J.; Bauer, H.; Pahl, J.; Maron, L.; Harder, S. Calcium Hydride Catalyzed Highly 1,2-Selective Pyridine Hydrosilylation. *Chem. - Eur. J.* **2015**, *21*, 11452−11461.

(8) (a) Radcliffe, J. E.; Dunsford, J. J.; Cid, J.; Fasano, V.; Ingleson, M. J. N-Heterocycle-Ligated Borocations as Highly Tunable Carbon Lewis Acids. *Organometallics* **2017**, *36*, 4952−4960. (b) McGough, J. S.; Butler, S. M.; Cade, I. A.; Ingleson, M. J. Highly Selective Catalytic Trans-hydroboration of Alkynes Mediated by Borenium Cations and $B(C_6F_5)_3$. *Chem. Sci.* **2016**, *7*, 3384−3389. (c) Fasano, V.; Radcliffe, J. E.; Ingleson, M. J. $B(C_6F_5)_3$ Catalyzed Reductive Amination using Hydrosilanes. *ACS Catal.* **2016**, *6*, 1793−1798.

(9) (a) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. Electronically Unsaturated Three-Coordinate Aluminum Hydride and Organoaluminum Cations. *Chem. - Eur. J.* **2018**, *24*, 4794−4799. (b) Jakhar, V. K.; Barman, M. K.; Nembenna, S. Aluminum Monohydride Catalyzed Selective Hydroboration of Carbonyl Compounds. *Org. Lett.* **2016**, *18*, 4710−4713. (c) Nikonov, G. I. New Tricks for an Old Dog: Aluminum Compounds as Catalysts in Reduction Chemistry. *ACS Catal.* **2017**, *7*, 7257−7266. (d) Weetman, C.; Inoue, S. The Road Travelled: After Main-Group Elements as Transition Metals. *ChemCatChem* **2018**, *10*, 4213−4228. (e) Dagorne, S.; Wehmschulte, R. Recent Developments on the Use of Group 13 Metal Complexes in Catalysis. *ChemCatChem* **2018**, *10*, 2509−2520. (f) Leitao, E. M.; Manners, I. Catalysis in Service of Main Group Chemistry Offers a Versatile Approach to *p*-block Molecules and Materials. *Nat. Chem.* **2013**, *5*, 817−829.

(10) (a) Walker, J. C.; Klare, H. F.; Oestreich, M. Cationic Silicon Lewis Acids in Catalysis. *Nat. Rev. Chem.* **2020**, *4*, 54−62. (b) Kobayashi, S.; Kiyohara, H.; Yamaguchi, M. Catalytic Silicon-Mediated Carbon−Carbon Bond-Forming Reactions of Unactivated Amides. *J. Am. Chem. Soc.* **2011**, *133*, 708−711.

(11) (a) Bayne, J. M.; Stephan, D. W. Phosphorus Lewis Acids: Emerging Reactivity and Applications in Catalysis. *Chem. Soc. Rev.* **2016**, *45*, 765−774. (b) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. Olefin Isomerization and Hydrosilylation Catalysis by Lewis Acidic Organofluorophosphonium Salts. *J. Am. Chem. Soc.* **2013**, *135*, 18308−18310. (c) Chitnis, S. S.; LaFortune, J. H. W.; Cummings, H.; Liu, L. L.; Andrews, R.; Stephan, D. W. Phosphorus Coordination Chemistry in Catalysis: Air Stable P(III)-Dications as Lewis Acid Catalysts for the Allylation of C−F Bonds. *Organometallics* **2018**, *37*, 4540−4544. (d) Hynes, T.; Welsh, E. N.; McDonald, R.; Ferguson, M. J.; Speed, A. W. H. Pyridine Hydroboration with a Diazaphospholene Precatalyst. *Organometallics* **2018**, *37*, 841−844.

(12) (a) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. Alkali Metal Hydridotriphenylborates $[(L)M][HBPh_3]$ (M = Li, Na, K): Chemoselective Catalysts for Carbonyl and CO_2 Hydroboration. *J. Am. Chem. Soc.* **2016**, *138*, 10790−10793. (b) Osseili, H.; Mukherjee, D.; Spaniol, T. P.; Okuda, J. Ligand Influence on Carbonyl Hydroboration Catalysis by Alkali Metal Hydridotriphenylborates $[(L)M][HBPh_3]$ (M = Li, Na, K). *Chem. - Eur. J.* **2017**, *23*, 14292−14298.

(13) (a) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. Direct Observation of a Borane-Silane Complex Involved in Frustrated Lewis-Pair-Mediated Hydrosilylations. *Nat. Chem.* **2014**, *6*, 983−988. (b) Piers, W. E.; Marwitz, A. J.; Mercier, L. G. Mechanistic Aspects of Bond Activation with Perfluoroarylboranes. *Inorg. Chem.* **2011**, *50*, 12252−12262.

(14) (a) Chen, J.; Lalancette, R. A.; Jäkle, F. Synthesis and Lewis Acid Properties of a Ferrocene-Based Planar-Chiral Borenium Cation. *Chem. Commun.* **2013**, *49*, 4893−4895. (b) Bamford, K. L.; Qu, Z. W.; Stephan, D. W. Activation of H_2 and Et_3SiH by the Borinium Cation $[Mes_2B]^+$: Avenues to Cations $[MesB(\mu\text{-}H)_2(\mu\text{-}Mes)BMes]^+$ and $[H_2B(\mu\text{-}H)(\mu\text{-}Mes)B(\mu\text{-}Mes)(\mu\text{-}H)BH_2]^+$. *J. Am. Chem. Soc.* **2019**, *141*, 6180−6184. (c) Eisenberger, P.; Crudden, C. M. Borocation Catalysis. *Dalton Trans.* **2017**, *46*, 4874−4887. (d) Denmark, S. E.; Ueki, Y. Lewis Base Activation of Lewis Acids: Group 13. In Situ Generation and Reaction of Borenium Ions. *Organometallics* **2013**, *32*, 6631−6634.

(15) Three main types of mononuclear monocationic boron complexes, which differ from one another in coordination number around the boron center, have been studied: (borinium, $[R_2B]^+$;

borenium, $[(L)R_2B]^+$; boronium, $[(L)_2R_2B]^+$). For further details see: (a) Koelle, P.; Noeth, H. The Chemistry of Borinium and Borenium Ions. *Chem. Rev.* **1985**, *85*, 399−418. (b) De Vries, T. S.; Prokofjevs, A.; Vedejs, E. Cationic Tricoordinate Boron Intermediates: Borenium Chemistry from the Organic Perspective. *Chem. Rev.* **2012**, *112*, 4246−4282. (c) Piers, W. E.; Bourke, S. C.; Conroy, K. Borinium, Borenium and Boronium Ions: Synthesis, Reactivity, and Application. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016−5036.

(16) The expected trend of Lewis acidity, on the basis of the coordination number around the boron center is borinium > borenium > boronium. For further details see: (a) Inés, B.; Patil, M.; Carreras, J.; Goddard, R.; Thiel, W.; Alcarazo, M. Synthesis, Structure and Reactivity of a Dihydridoborenium Cation. *Angew. Chem., Int. Ed.* **2011**, *50*, 8400−8403. (b) Tsai, J. H.; Lin, S. T.; Yang, R. B.; Yap, G. P.; Ong, T. G. Two-Way Street Transformation of Boronium and Borane Complexes Facilitated by Amino-Linked N-Heterocyclic Carbene. *Organometallics* **2010**, *29*, 4004−4006. (c) Someya, C. I.; Inoue, S.; Präsang, C.; Irran, E.; Driess, M. Formation of N-Heterocyclic Donor-Stabilized Borenium Ions. *Chem. Commun.* **2011**, *47*, 6599−6601. (d) Cowley, A. H.; Lu, Z.; Jones, J. N.; Moore, J. A. Synthesis and Structure of a Boron Cation Supported by a *β*-Diketiminate Ligand. *J. Organomet. Chem.* **2004**, *689*, 2562−2564. (e) Shoji, Y.; Tanaka, N.; Mikami, K.; Uchiyama, M.; Fukushima, T. A Two-coordinate Boron Cation Featuring $C-B^+-C$ Bonding. *Nat. Chem.* **2014**, *6*, 498−503. (f) Muthaiah, S.; Huan Do, D. C.; Ganguly, R.; Vidović, D. Counterion Dependence on the Synthetic Viability of NHC-Stabilized Dichloroborenium Cations. *Organometallics* **2013**, *32*, 6718−6724. (g) Tay, M. Q.; Murugesapandian, B.; Lu, Y.; Ganguly, R.; Rei, K.; Vidović, D. Dihaloborenium Cations Stabilized by a Four-Membered N-Heterocyclic Carbene: Electron Deficiency Compensation by Asymmetric Structural Changes. *Dalton Trans.* **2014**, *43*, 15313−15316. (h) Vidovic, D.; Reeske, G.; Findlater, M.; Cowley, A. H. Synthesis and Structures of Boron Dihalides Supported by the C_6F_5-Substituted *β*-diketiminate Ligand $[HC(CMe)_2(NC_6F_5)_2]^-$. *Dalton Trans.* **2008**, 2293−2297. (i) Gates, D. P.; McWilliams, A. R.; Ziembinski, R.; Liable-Sands, L. M.; Guzei, I. A.; Yap, G. P.; Rheingold, A. L.; Manners, I. Chemistry of Boratophosphazenes: Synthesis of Borazine−Phosphazene Hybrid Cations, and New Inorganic Heterocycles by Skeletal Substitution Reactions. *Chem. - Eur. J.* **1998**, *4*, 1489−1503.

(17) (a) Vargas-Baca, I.; Findlater, M.; Powell, A.; Vasudevan, K. V.; Cowley, A. H. Boron di- and tri-cations. *Dalton Trans.* **2008**, *45*, 6421−6426. (b) Dinda, R.; Ciobanu, O.; Wadepohl, H.; Hübner, O.; Acharyya, R.; Himmel, H.-J. Synthesis and Structural Characterization of a Stable Dimeric Boron(II) Dication. *Angew. Chem., Int. Ed.* **2007**, *46*, 9110−9113. (c) Shen, C. T.; Liu, Y. H.; Peng, S. M.; Chiu, C. W. A Di-substituted Boron Dication and its Hydride-induced Transformation to an NHC-Stabilized Borabenzene. *Angew. Chem., Int. Ed.* **2013**, *52*, 13293−13297. (d) Litters, S.; Kaifer, E.; Enders, M.; Himmel, H. J. A Boron−Boron Coupling Reaction Between Two Ethyl Cation Analogues. *Nat. Chem.* **2013**, *5*, 1029−1034. (e) Ghadwal, R. S.; Schürmann, C. J.; Andrada, D. M.; Frenking, G. Mono-and Di-Cationic Hydrido Boron Compounds. *Dalton Trans.* **2015**, *44*, 14359−14367. (f) Lee, W.-H.; Lin, Y.-F.; Lee, G.-H.; Peng, S.-M.; Chiu, C.-W. N-Heterocyclic Olefin Stabilized Boron Dication. *Dalton Trans.* **2016**, *45*, 5937−5940.

(18) (a) Farrell, J. M.; Hatnean, J. A.; Stephan, D. W. Activation of Hydrogen and Hydrogenation Catalysis by a Borenium Cation. *J. Am. Chem. Soc.* **2012**, *134*, 15728−15731. (b) Farrell, J. M.; Posaratnanathan, R. T.; Stephan, D. W. A family of N-Heterocyclic Carbene-Stabilized Borenium Ions for Metal-Free Imine Hydrogenation Catalysis. *Chem. Sci.* **2015**, *6*, 2010−2015. (c) Tsurumaki, E.; Sung, J.; Kim, D.; Osuka, A. Subporphyrinato Boron(III) Hydrides. *J. Am. Chem. Soc.* **2015**, *137*, 1056−1059.

(19) Lawson, J. R.; Clark, E. R.; Cade, I. A.; Solomon, S. A.; Ingleson, M. J. Haloboration of Internal Alkynes with Boronium and Borenium Cations as a Route to Tetrasubstituted Alkenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 7518−7522.

(20) Bonnier, C.; Piers, W. E.; Parvez, M.; Sorensen, T. S. Borenium Cations Derived from BODIPY Dyes. *Chem. Commun.* **2008**, 4593−4595.

(21) Vidovic, D.; Findlater, M.; Cowley, A. H. A *β*-Diketiminate-Supported Boron Dication. *J. Am. Chem. Soc.* **2007**, *129*, 8436−8437.

(22) Jaiswal, K.; Prashanth, B.; Ravi, S.; Shamasundar, K. R.; Singh, S. Reactivity of a Dihydroboron Species: Synthesis of a Hydroborenium Complex and an Expedient Entry into Stable Thioxo- and Selenoxo-Boranes. *Dalton Trans.* **2015**, *44*, 15779−15785.

(23) Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. The Elusive Three-Coordinate Dicationic Hydrido Boron Complex. *J. Am. Chem. Soc.* **2014**, *136*, 914−917.

(24) Jaiswal, K.; Prashanth, B.; Singh, S. Fine-Tuning of Lewis Acidity: The Case of Borenium Hydride Complexes Derived from Bis(phosphinimino)amide Boron Precursors. *Chem. - Eur. J.* **2016**, *22*, 11035−11041.

(25) Dyson, P. J.; Jessop, P. G. Solvent Effects in Catalysis: Rational Improvements of Catalysts via Manipulation of Solvent Interactions. *Catal. Sci. Technol.* **2016**, *6*, 3302−3316.

(26) Banerjee, S.; Vanka, K. $B(C_6F_5)_3$: Catalyst or Initiator? Insights from Computational Studies into Surrogate Silicon Chemistry. *ACS Catal.* **2018**, *8*, 6163−6176.

(27) Ashley, A. E.; Thompson, A. L.; O'Hare, D. Non-Metal-Mediated Homogeneous Hydrogenation of CO_2 to CH_3OH. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839−9843.

(28) Rauch, M.; Parkin, G. Zinc and Magnesium Catalysts for the Hydrosilylation of Carbon Dioxide. *J. Am. Chem. Soc.* **2017**, *139*, 18162−18165.

(29) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Frohlich, R.; Grimme, S.; Stephan, D. W. Rapid Intramolecular Heterolytic Dihydrogen Activation by a Four-Membered Heterocyclic Phosphane−Borane Adduct. *Chem. Commun.* **2007**, *47*, 5072−5074.

(30) Sumerin, V.; Schulz, F.; Nieger, M.; Leskel, M.; Repo, T.; Rieger, B. Facile Heterolytic H_2 Activation by Amines and $B(C_6F_5)_3$. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001−6003.

(31) Zwettler, N.; Walg, S. P.; Belaj, F.; Mösch-Zanetti, N. C. Heterolytic Si-H Bond Cleavage at a Molybdenum-Oxido-Based Lewis Pair. *Chem. - Eur. J.* **2018**, *24*, 7149−7160.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian09, Rev. C.01*; Gaussian, Inc., Wallingford, CT, 2010.

(33) Chemcraft-graphical software for visualization of quantum chemistry computations; https://www.chemcraftprog.com.

(34) Schaftenaar, G.; Vlieg, E.; Vriend, G. Molden 2.0: quantum chemistry meets proteins. *J. Comput.-Aided Mol. Des.* **2017**, *31*, 789.