Progressing Frustrated Lewis Pair Abilities of NHC/GaR_3 Combinations for Catalytic Hydroboration of Unsaturated Organic Molecules

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ABSTRACT Exploiting the steric incompatibility of the trisalkylgallium GaR_3 (R = CH_2SiMe_3) and I*t*Bu (1,3-di-tert-butylimidazol-2-ylidene) and the bulky N-heterocyclic carbene 1,3-bis(tert-butyl)imidazol-2-ylidene (ItBu), here we report the B-H bond activation of pinacolborane which

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has led to the isolation and structural authentication of a novel ion pair $\{I\textit{t}Bu\text{-}BPin\}^{+}\{GaR_3(\mu\text{-}H)GaR_3\}^{-}$] (**2**). Contrastingly, neither I*t*Bu or GaR_3 were able to react with HBpin under the conditions of this study. Combing a NHC-stabilized borenium cation with an anionic dinuclear gallate, **2** proved to be unstable in solution at room temperature, evolving to the abnormal NHC-Ga complex [$BPin\{\{N(\textit{t}Bu)]_2CHCGa(R)_3\}$] (**3**). Formation of **3** can be attributed to the formal deprotonation of the cation present in **2** by its gallate hydride counterion, with concomitant H_2 and GaR_3 elimination. Interestingly, the structural isomer of **2**, with the borenium cation residing at the C4 position of the carbene [$\{\textit{a}ItBu\text{-}BPin\}^{+}\{GaR_3(\mu\text{-}H)GaR_3\}^{-}$] (**4**) is obtained when the abnormal NHC complex [$\textit{a}I\textit{t}Bu\cdot GaR_3$] (**1**) is heated at 70°C with HBpin, demonstrating that under these forcing conditions it is possible to induce thermal frustration of the Lewis base/ Lewis acid components of **1**, enabling the activation of HBpin. Building on these stoichometric studies, the FLP reactivity observed for the GaR_3/I*t*Bu combination with HBpin could then be upgraded to catalytic regimes, allowing the efficient hydroboration of a ranges of ketones and aldehydes under mild reaction conditions. Combining reactivity studies with kinetic investigations a cooperative mechanism is proposed where the hydroboration process is favored by the formation of a highly nucleophilc hydride gallate species, whereas the electrophilicity of the organic substrates is enhanced by the coordination of a borenium cation.

Introduction

Since the inception of Frustrated Lewis Pair (FLP) chemistry,[1] sterically incompatible Lewis acid/base pairings have become a powerful and widespread protocol for the activation of small molecules.[2] Recent years have seen significant application of FLP-reactivity within transition-metal free hydrogenation reactions, with the ability to operate under catalytic conditions.[3] The unique reactivity of these systems is routed through their incurred frustration, where the formation

of a classical Lewis adduct is completely precluded as a direct consequence of steric encumbrance. Some of the most popular FLP systems have been modelled from phosphine/borane combinations. Typical boranes employed contained electron withdrawing perfluorinated arene substituents (Ar^F) which greatly increase their Lewis acidity and impose steric constraints.[4] Notwithstanding, deviation from phosphine/borane systems is also possible. Thus N-heterocyclic carbenes (NHCs) or bulky amines such as TMP(H) have also emerged as powerful Lewis basic partners of $B(Ar^F)_3$, displaying excellent FLP capabilities for small molecule activation.[5] In an analogous manner, alternative Lewis acids to tris(aryl)boranes normally involve the use of aluminium,[6] whereas gallium has been significantly less employed.[7] Recently we have shown that by combining the particularly bulky and basic N-heterocyclic carbene I*t*Bu (1,3-di-tert-butylimidazol-2-ylidene) with a tris(alkyl) gallium GaR_3 ($R = CH_2SiMe_3$) it is possible to activate unsaturated organic molecules such as ketones and aldehehydes (via C=O insertion)[8] as well as the cleavage X-H acidic bonds of alcohols, amines and acetylenes to name just a few.[9] Combining structural studies with NMR monitoring of the reactions and DFT calculations, these studies shed new light on the possible mechanisms involved in C=O reduction processes, where the NHC can act as a Lewis base not only via its *normal* C2 position (kinetic product) but also via its C4 (*abnormal*) site (thermodynamic product). This isomerisation seems to be driven by the relief of the steric hindrance around the former C=O group.[10] Evidencing the synergistic behaviour of these NHC/GaR_3 pairings, when separated none of the components is able to activate these ketones or aldehydes on its own. Building on these studies, here we assess the capabilities of the I*t*Bu/GaR_3 combination to induce the activation of hydridic hydrogens using HBPin as a model substrate. Furthermore, we also investigate its ability to operate under catalytic conditions to facilitate hydroboration processes of carbonyl compounds.

Involving the direct addition of a B-H bond across unsaturated organic compounds (i.e. alkenes, alkynes or carbonyl derivatives), hydroboration catalysis has gained increasing importance in synthesis, becoming a fundamental tool to access organoborane compounds.[11] While a large number of these studies used transition metal complexes as catalysts, the last decade has witnessed several examples of s- and p-block metal hydrides (Figure 1a) emerge as competent hydroboration catalysts towards a variety of unsaturated substrates, with the vast majority of these studies using HBPin as the borane of choice.[12-17] For carbonyl-based substrates, these reactions are generally accepted to proceed through an initial insertion of the substrate across the metal-hydride bond, leading to an alkoxide intermediate. A σ-bond metathesis step can then ensue promoted by the stoichiometric excess of HBPin present, leading to the final product with regeneration of the active hydride catalyst. Metal-free examples have also been established in recent years, with examples from Stephan[18] and Oestreich[19] which have shown that electrophilic boranes such as Piers's borane [$HB(C_6F_5)_2$], $B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_3$ can catalyze the hydroboration of alkenes and alkynes with HBPin (Figure 1b). This approach has also been used for hydroboration of imines, ketones, aldehydes and alkynes.[20] Not limited to single component systems, the combination of highly Lewis acidic boranes, such as tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, in the presence of a Lewis base (LB), can lead to the abstraction of the hydride from HBPin to form [$HB(C_6F_5)_3$] and the borenium cation $[LB{\cdot}BPin]^+$, with the latter being actually the active catalyst of the hydroboration process as shown by Crudden when using DABCO (1,4-diazabicyclo[2.2.2]octane) as a LB for the hydroboration of imines (Figure 1c).[21] Other systems with FLP capabilities such as dimethylxanthene-based phosphine/borane shown in Figure 1c developed by Aldridge which can act as a precatalyst for the hydroboration of alkynes.[22]

Herein we investigate the catalytic ability of a novel gallium hydride species (Figure 1d) obtained by the activation of HBPin by the I*t*Bu/GaR_3 (*vide infra*) to facilitate the hydroboration of ketones, aldehydes and imines. Through the isolation of key reaction intermediates and kinetic studies we provided mechanistic insights on how these processes may take place.

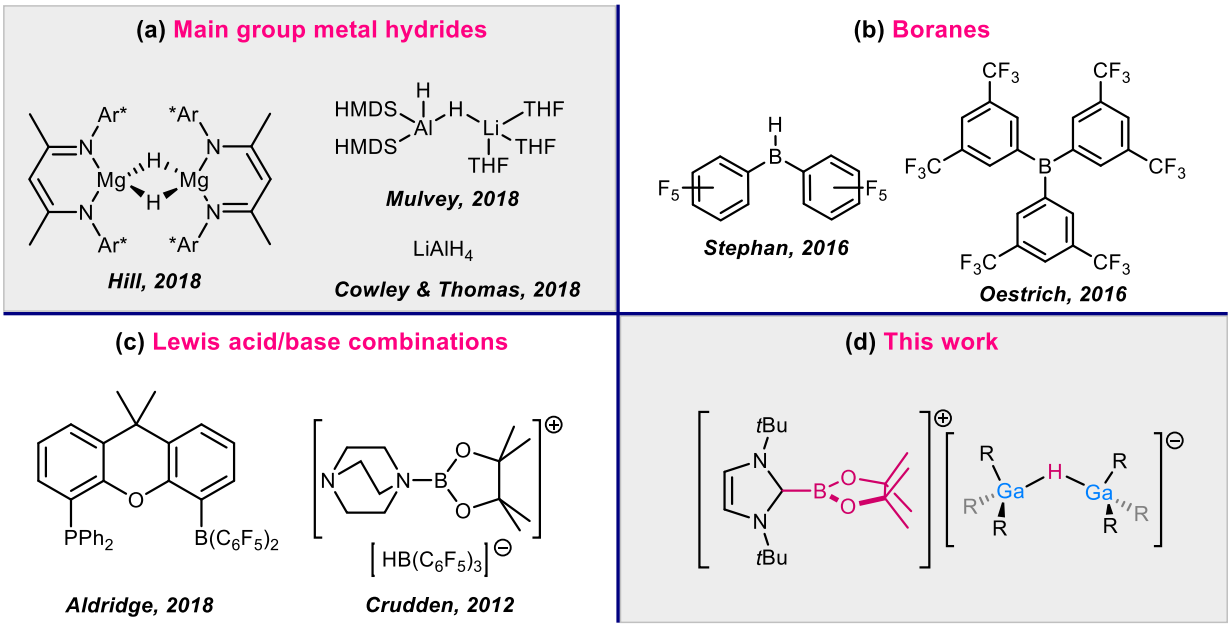
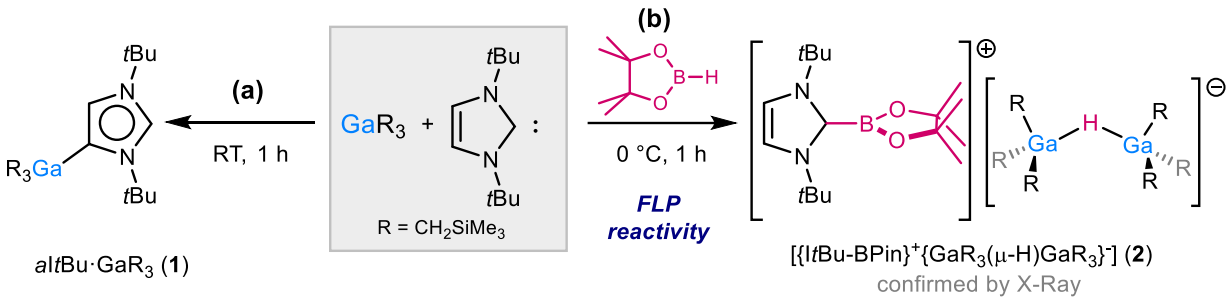


Figure 1 Selected examples of main-group catalytic approaches for hydroboration reactions. Ar* = 2,6-(iPr)$_2$-C_6H_3, HMDS = $N(SiMe_3)_2$

Results and Discussion

Taking heed from our previous studies,[23] combining equimolar amounts of GaR_3 and I*t*Bu in a non-polar solvent at room temperature instantly leads to the formation of a stable, abnormal NHC/Ga complex, *a*I*t*Bu·GaR_3 (**1**). The structure of **1** was established by X-ray crystallographic studies (see ESI) and it can be considered as a deactivation product as at room temperature it is a very robust species which shows no dissociation or further FLP reactivity. However, in our previous studies we discovered that its formation can be minimized by lowering the reaction

temperature to 0 °C. Introducing a suitable substrate under these conditions, could then promote its subsequently activation (via X-H activation or C=O insertion).[8,9] Thus, we started our stoichiometric studies by reacting HBPin with equimolar amounts of GaR_3 and I*t*Bu at 0 °C for 1 h in hexane. Cooling of the solution at -30 °C led to the isolation of the borenium gallate complex $[\{I tBu\text{-}BPin\}^+\{GaR_3(\mu\text{-}H)GaR_3\}^-]$ (**2**) which was characterized by X-ray crystallographic analysis and can be envisaged as the result of the FLP-splitting of the B-H bond of the borane. Formation of **2** is clearly synergic in terms that, under the conditions of the study, no apparent reaction of the single components is observed with HBpin. For I*t*Bu, not even coordination to B is observed, whereas GaR_3 slowly generates RBpin over time long periods of time at room temperature (45% conversion after 2 days). This sluggish reactivity contrasts with that reported by Cowley for $AlEt_3$ which reacts instantaneously to give $AlEt_2H$ and EtBpin.[17a]



Scheme 1 (a) Synthesis of *a*I*t*Bu·GaR_3 (**1**). (b) Synthesis of $[\{I tBu\text{-}BPin\}^+\{GaR_3(\mu\text{-}H)GaR_3\}^-]$ (**2**) via FLP-splitting of HBPin

Compound **2** consists of a cationic NHC-BPin fragment with the boron residing on the C2-position of the carbene (C(25) in Scheme 1). Both C and B atoms exhibit trigonal planar environments (sum of angles around C(25) and B(1), 359.75 ° and 359.98 ° respectively). The length of the B(1)-C(25) bond [1.588(3) Å] is consistent with those reported in the literature for related NHC-stabilized bis(aryl)borenium cations.[24] Unsurprisingly, this B-C bond distance is noticeably shorter

than that recently reported by Mandal for a coordination adduct between a tetra-substituted abnormal NHC and HBPin [1.668(2) Å] which can be rationalized considering the higher coordination number of B in the latter and its neutral character in comparison with the borenium cation.[25] Considering the perpendicular binding of BPin to the NHC, similarities can be drawn to an example reported by Vidovíc, where I*t*Bu is used to stabilize a catecholatoborenium cation, $\{BCat^{+}\}$, with charge balance achieved by a $\{B(3,5\text{-}Cl_2\text{-}C_6H_3)_4\}^{-}$ anion.[26] The authors comment that the side-on arrangement of the borenium to the NHC allows for electrostatic interactions between Me groups of the NHC's *t*Bu-substituents and the cationic boron atom, with an average distance of 2.846 Å. Within **2**, it is therefore likely that orthogonal binding of $\{BPin\}^{+}$ to the NHC maximizes the opportunity for stabilization of the borocation via interaction of the *t*Bu groups to the empty p-orbital of boron with detected distances of 3.081(4) and 3.028(3) Å from the crystallographic data.

While discussions thus far have labelled $\{I\textit{t}Bu\text{-}BPin\}^{+}$ as a borenium cation, it could also be formally considered as a boryl-imidazolium cation (Scheme 2). Previous theoretical studies by Stephan have focused on a constitutionally-analogous species to **2**, reached by FLP-activation of catecholborane (HBCat) by $\textit{t}Bu_3P$ and $B(C_6F_5)_3$, leading to the ion pair $[\{\textit{t}Bu_3P\text{-}BCat\}^{+}\{HB(C_6F_5)_3\}^{-}]$.[4a] Natural Bond Order (NBO) calculations then defined the charge of the cation to formally lie on the P atom, rendering the species as a boryl-phosphonium rather than a phosphine-stabilized borenium cation. Although a similar understanding could be applied to the cation of **2**, onward reactivity (*vide infra*) of our system indicates that recognizing $\{I\textit{t}Bu\text{-}BPin\}^{+}$ as a borenium cation is more representative of its succeeding behavior.

Scheme 2 Borenium and imidazolium representations of $\{I\textit{t}Bu\text{-}BPin\}^{+}$ of **2**

The counterion for this structure is a dinuclear gallate comprising two GaR_3 units connected by a bridging hydride. The structure of this anion is closely related to that reported by Stephan for ($\{Ga(C_6F_5)_3(\mu\text{-}H)Ga(C_6F_5)_3\}^-$) which is part of a phosphonium gallate resulting from the FLP-cleavage of H_2 by a 2:1 combination of $Ga(C_6F_5)_3$ and P*t*Bu$_3$.[27] Interestingly, regardless of 1:1:1 stoichiometry applied, in our case, the anionic fragment consistently forms with two equivalents of GaR_3 which we propose to be a crystallization feature for improved stability of the metal hydride species.[28]

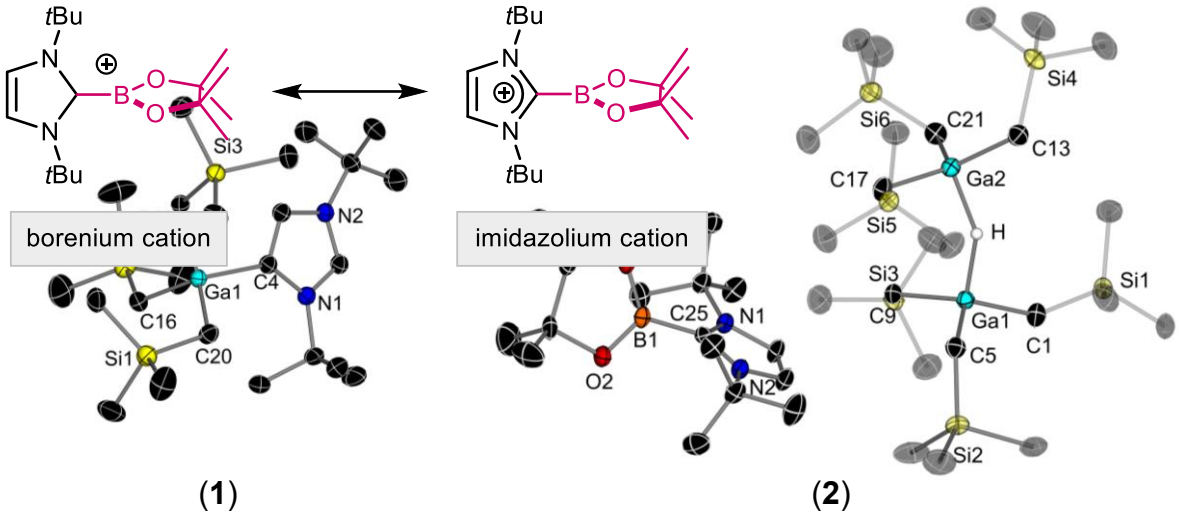
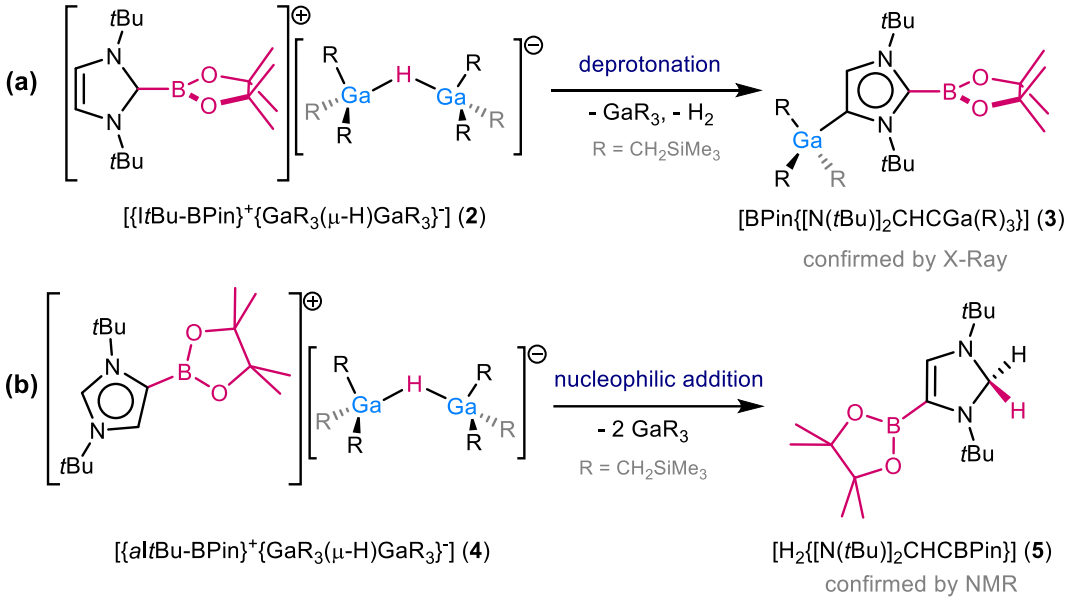


Figure 2 Molecular structures of *a*I*t*Bu·GaR_3 (**1**) and [$\{$I*t*Bu-BPin$\}^+\{GaR_3(\mu\text{-}H)GaR_3\}^-$] (**2**) with displacement ellipsoids at 50% probability and all hydrogen atoms omitted for clarity, with the exception of bridging hydride of **2**. $SiMe_3$ groups draws at 70% transparency for clarity Selected bond angles (°) and distances (Å) of **1**: C(12)-Ga(1)-C(16) 108.96(7), C(12)-Ga(1)-C(20) 112.18(8), C(12)-Ga(1)-C(4) 103.09(7), C(16)-Ga(1)-C(2) 110.70(7), C(16)-Ga(1)-C(4) 108.29(7), C(20)-Ga(1)-C(4) 113.27(7), Ga(1)-C(12) 2.0255(17), Ga(1)-C(16) 2.0231(18), Ga(1)-C(20) 2.0154(18), Ga(1)-C(4) 2.0771(17). Selected bond angles (°) and distances (Å) of **2**: O(1)-B(1)-C(25) 120.46(19), O(2)-B(1)-C(25) 123.79(19), O(2)-B(1)-O(2) 115.73(19), N(1)-C(25)-B(1) 126.47(18), N(1)-C(25)-N(2) 107.35(17), B(1)-C(25)-N(2) 125.92(19), Ga(1)-C(1) 2.004(2), Ga(1)-C(5) 2.010(2), Ga(1)-C(9) 2.012(2), B(1)-C(25) 1.588(3).

While the synthesis and solid-state determination of **2** by X-ray crystallography is reproducible, its isolation at room temperature as a crystalline solid and solution-state characterization proved particularly challenging with multiple attempts resulting in decomposition products. Deeper analysis of this decomposition revealed the inevitable formation of an unexpected abnormal NHC-

Ga complex, [BPin{{N(*t*Bu)]$_2$CHCGa(R)$_3$}] (**3**) which can be recrystallized in a 17 % yield. Its most salient NMR feature is a singlet at δ 7.32 ppm in the ^{1}H NMR in C_6D_6 for the remaining H on the imidazole ring, alongside the inequivalence of both *t*Bu groups (at δ 1.64 and 1.26 ppm). In addition, a resonance at δ 160.3 ppm is observed in the ^{13}C NMR spectrum for its carbenic carbon, a similar chemical shift to that observed for **1** (δ 159.5 ppm) whereas its ^{11}B NMR shows a broad resonance at δ 26.8 ppm which compares well with neutral, BPin-Csp^2 environments.[20b] The structure of **3** could also be established by X-ray crystallographic studies (Figure 3). The coordination features around Ga are similar to those found in **1**, with similar $C_{carbenic}$-Ga distances [2.0771(17) and 2.0852(15) Å respectively] whereas the B-C(2) distance [1.591(2) Å] is almost identical to that found in **2**. While the decomposition of **2** into **3** could not be monitored by NMR, when analyzing isolated samples of **3** by ^{1}H NMR, variable amounts of GaR_3 could also be detected (see ESI). A possible explanation for the formation of **3** could be the deprotonation of the imidazole backbone of **2** by the {GaR_3-(μ-H)-GaR_3}$^-$ fragment, producing a carbenic center at the C(4)-position to which GaR_3 can then bind with subsequent H_2 elimination (Scheme 3a). This is somewhat surprising as gallium hydrides are expected to be poor bases but perhaps its anionic constitution enhances its basicity. No evidence could be found to support the deprotonation of the imidazole backbone by one of the monosilyl groups on Ga, which is consistent with the previously noted low kinetic basicity of these alkyls groups when coordinated to Ga.[9, 29]



Scheme 3 (a) Decomposition pathway of **2** into **3** by deprotonation of imidazole backbone. (b) Decomposition of **4** into **5** by nucleophilic addition across C(2)-position of imidazole fragment

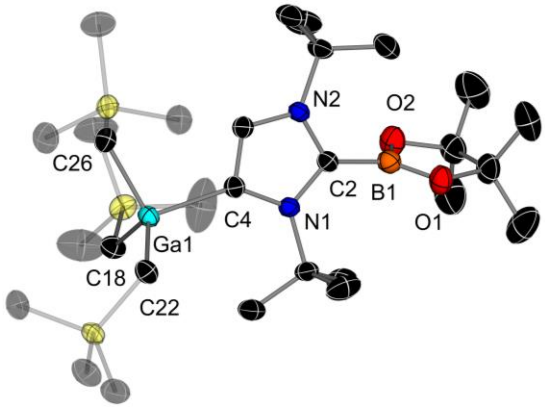


Figure 3 Molecular structure of [BPin{[N(*t*Bu)]2CHCGa(R)3}] (**3**) with displacement ellipsoids at 50% probability and hydrogen atoms omitted for clarity. SiMe3 groups draws at 70% transparency for clarity. Selected bond angles (°) and distances (Å): N(2)-C(2)-N(1) 106.79(12), N(2)-C(2)-B(1) 123.65(12), N(1)-C(2)-B(1) 128.54(13), O(2)-B(1)-C(2) 119.73(15), O(2)-B(1)-O(1) 115.27(15), C(2)-B(1)-O(1) 125.00(15), C(2)-B(1) 1.591(2), Ga(1)-C(4) 2.0852(2)

As mentioned above, our previous studies have found that *a*I*t*Bu·GaR$_3$ (**1**) is deactivated towards exhibiting further FLP reactivity. A similar behavior has been reported by Tamm for related *a*I*t*Bu·B(C$_6$F$_5$)$_3$.[30] Interestingly, while **1** is inert towards HBPin at room temperature, we found that increasing the reaction temperature to 70 °C for 4 h allowed for formation of the mixed borenium

gallate [{*a*ItBu-BPin}$^{+}${GaR_3(μ-H)GaR_3}$^{-}$] (**4**) (Figure 4). Compound **4** was subjected to Hirshfeld Atom Refinement (HAR),[32,33] using the NoSpherA2.[34] As shown previously,[35] HAR allows for the position of the bridging hydride to be defined, as well as discussion of its associated bond lengths and angles. Further details can be found in the ESI.[36]

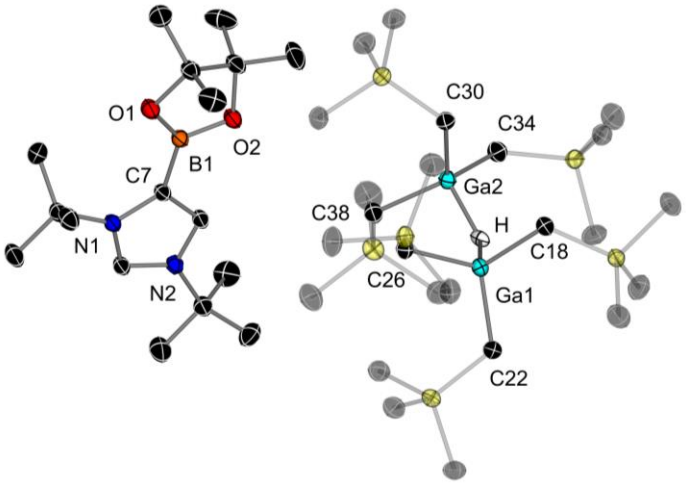


Figure 4 Molecular structure of [{*a*I*t*Bu-BPin}$^{+}${GaR_3(μ-H)GaR_3}$^{-}$] (**4**) with displacement ellipsoids at 50% probability with hydrogen atoms omitted for clarity, with the exception of bridging hydride atoms. $SiMe_3$ groups have been drawn at 70% transparency for clarity. Selected bond angles (°) and distances (Å) for **4**: Ga(1)-H-Ga(2) 134.6(9), O(1)-B(1)-C(7) 129.24(10), O(1)-B(1)-O(2) 114.39(10), C(7)-B(1)-O(2) 116.35(10), B(1)-C(7)-N(1) 133.86(9), B(1)-C(7)-C(8) 120.53(9), N(1)-C(7)-C(8) 105.61(9), H-Ga(1)-C(26) 107.3(5), H-Ga(1)-C(22) 102.0(5), H-Ga(1)-C(18) 102.0(5), C(26)-Ga(1)-C(22) 114.41(5), C(26)-Ga(1)-C(18) 115.74(5), Ga(1)-H-Ga(2) 134.6(9), B(1)-C(7) 1.5648(15), Ga(1)-C(26) 2.0201(11), Ga(1)-C(22) 2.0156(11), Ga(1)-C(18) 2.0177(11), Ga(1)-H 1.783(16), Ga(2)-H 1.770(17)

The dinuclear gallate anionic fragment in **4** is identical to that found in **2** but since HAR could be applied to this structural determination, discussion of its most salient structural parameters is included here. It comprises two GaR_3 units connected by a bridging hydride, where each gallium center adopts a distorted tetrahedral geometry (mean bond angles around Ga1 and Ga2, 109.16° and 109.29° respectively). The Ga1-H-Ga2 bond angle [134.6(9)°] is noticeably more acute than that reported by Stephan for a phosphonium gallate [{$Ga(C_6F_5)_3$(μ-H)$Ga(C_6F_5)_3$}$^{-}$]

[175(2)°].[27] It should be noted that are currently only a few structurally defined anionic Ga(III) hydride species are known.[27,37] Related to the anion present in **2** and **4**, Uhl has reported the structure of neutral Np_2GaH (Np= CH_2CMe_3) which in the solid state exhibits a dimeric structural motif.[38] This gallate anion is balanced by a cation which can be considered as a structural isomer of the one present in **2**, where the BPin fragment now resides on the C4 position. A slight shortening of this bond is observed compared to its length in **2** [C(2)-BPin 1.588(3) Å (**2**) versus C(7)-BPin 1.5648 (15) Å (**4**)], reflecting the stronger σ-donor abilities of mesoionic carbenes and its lower steric demands.[39] Additionally, the BPin ring now resides in the same plane as the imidazole ring, as opposed to its perpendicular disposition in **2**. The unexpected formation of **4** can potentially be explained by the occurrence of thermally induced frustration succeeding breakage of the Ga-C bond at elevated temperatures, enabling the trapping of the C4-isomer by its reaction with HPin.[31] C2- and C4-bound isomers have been previously detected by us for the activation of 4-bromobenzaldehyde, where it was found that insertion of the aldehyde between the Lewis fragments was thermodynamically favored towards the C4-position.[8]

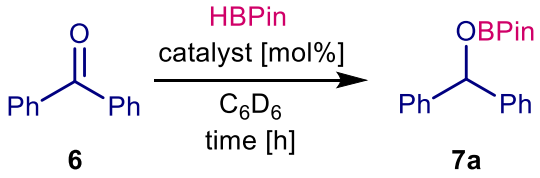
Interestingly, **4** also seems to be highly reactive in solution and attempts of characterizing this species by NMR spectroscopy by dissolving isolated crystals of **4** in C_6D_6 led to the observation of two equivalents of free GaR_3 along with a new set of resonances at δ 6.85, 4.40, 1.35 and 0.86 ppm, in a 1:2:9:9 ratio which we attribute to [H_2{[N(tBu)]$_2$CHCBPin}] (**5**) (Scheme 3b). The eventuality of **5** can be understood as a decomposition pathway of gallate **4**, where now the dinuclear gallate anion of the ion pair can act as a nucleophile towards the C2-position of the cationic fragment {*a*I*t*Bu-BPin}$^+$, formally reducing the cation and leading to neutral **5**.

Despite the observed decomposition pathways, the ability to form species **2** and **4** shows that these compounds are at least short lived in solution. Given that gallium hydrides have shown some

precedence within recent literature towards catalytic hydrogenation[27] and hydroboration reactions,[40] the presence of a Ga-H fragment within **2** lends potential for it to exhibit similar reductive behavior via hydroboration processes.

Choosing benzophenone (**6**) as a model substrate, early stages within the optimization studies revealed that the combined action of I*t*Bu and GaR_3 was necessary to promote hydroboration, with quantitative conversion to **7a** observed after 20 minutes at room temperature (entry 4). Lowering the catalyst loading to 5 mol% of each component (entry 5) allowed for >99% of **7a** to be formed after 3.5 h under ambient conditions. Demonstrating the catalytic superiority of the I*t*Bu and GaR_3 partnership, entry 6 shows that the NHC-GaR_3 stable C2-adduct, IPr·GaR_3 (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)[23] is unable to carry out the conversion, highlighting the need for the Lewis pair to be uncomplexed, though act cooperatively. The same outcome was observed with *a*I*t*Bu·GaR_3 (entry 7), however, increasing the reaction temperature to 70°C allowed for quantitative conversion to **7a** (entry 8). Altering the tris(alkyl)gallium for a less bulky, yet stronger Lewis acid ($GaCl_3$, entry 9) did not improve the efficiency of the reaction, reaffirming the value in the steric incompatibility between the Lewis acid and Lewis base components. Finally, the neutral abnormal NHC, **3**, was employed as a catalyst as it is the direct composition product of ion pair **2**. Hydroboration was observed to be very sluggish, suggesting it is unlikely to play a key role in mediating these reactions, under the conditions of this study.

Table 1 Catalyst screening for hydroboration of **6** by HBPin



6 **7a**

Entry	Catalyst	Loading [mol%]	Time [h]	Yield of 7a [%]

1	-	-	12	50[a]
2	GaR_3	5	3.5	30
3	I*t*Bu	5	2	16
4	I*t*Bu + GaR_3	10	0.3	>99
5	**I*t*Bu + GaR_3**	**5**	**3.5**	**>99**
6	IPr·GaR_3	5	3.5	3
7	*a*I*t*Bu·GaR_3	10	14	37
8	*a*I*t*Bu·GaR_3	5	1.5	>99[a]
9	I*t*Bu + $GaCl_3$	5	3.5	12
10	**3**	5	3.5	43

Reactions performed in a J. Young's NMR tube at 1 mmol scale in 0.5 mL C_6D_6. Yields determined against 10 mol% C_6Me_6 internal standard. [a] Reaction performed at 70 °C

Under the optimized conditions of 5 mol% of both GaR_3 and I*t*Bu, the protocol could be expanded towards a selection of ketones and aldehydes. Acetophenone was quantitatively transformed into **7b** within 2.5 h at room temperature; however, when pronounced steric bulk was introduced to the ketone *i.e.,* with 2,2-dimethylpropriophenone, the reaction time was seen to significantly increase to 19 h (**7c**, >99%). The high yields obtained for **7d** in just 30 minutes demonstrates halide tolerance within the catalysis as no interfering side reactions were detected. Highlighting the chemoselectivity of this process, introduction of a sensitive nitrile group (**7e**) sees the reaction occurring selectively at the carbonyl function – additionally, the reduced reaction time compared to **7a** could be a consequence of the electron withdrawing properties of the CN-functionality. Closing the ketone scope, aliphatic 2-butanone readily underwent hydroboration at room temperature in a short time (**7f**, 94%), and cylohexanone also displayed conversion into its analogous product (**7g**) in a respectable yield of 77%. A slight reduction in chemoselectivity was

observed with benzylideneacetone where, although the majority of hydroboration occurred in a 1,2-fashion across the carbonyl function (**7h**, 72%), a 10% yield of the product of addition across the alkene (**7h'**) was also observed by NMR spectroscopy (see ESI). Moving to cyclic α,β-unsaturated ketones (**7i** and **7j**), 1,4-hydroboration was exclusively achieved. We also exposed a selection of aldehydes to the catalytic conditions. Benzaldehyde, and its bromo-substituted derivatives, proved to undergo hydroboration very effectively and selectively at room temperature (**7k**-**7m**). Cinnamaldehyde proceeded with excellent chemoselectivity (contrasting with its ketone derivative) reaching 96% conversion into **7n** in just 40 minutes. The product from hydroboration of paraformaldehyde (**7o**) was obtained in a 70% yield after 3 hours at 70 °C.

We also assessed the ability of this NHC/GaR_3 system to catalyze the hydroboration of ethylbenzoate, which led to the cleavage of the C-O bond to generate **7p** and **7p'** in a 1:1 ratio. The reaction was carried out employing two equivalents of HBPin and a slight elevation of temperature (70^{o}C, see ESI for details). We were also successful in the quantitative hydroboration of *N*-benzylidineaniline creating a N-B bond in the process (**7q**, 99%) visible by ^{11}B NMR with the appearance of a broad singlet at δ 25.3 ppm.

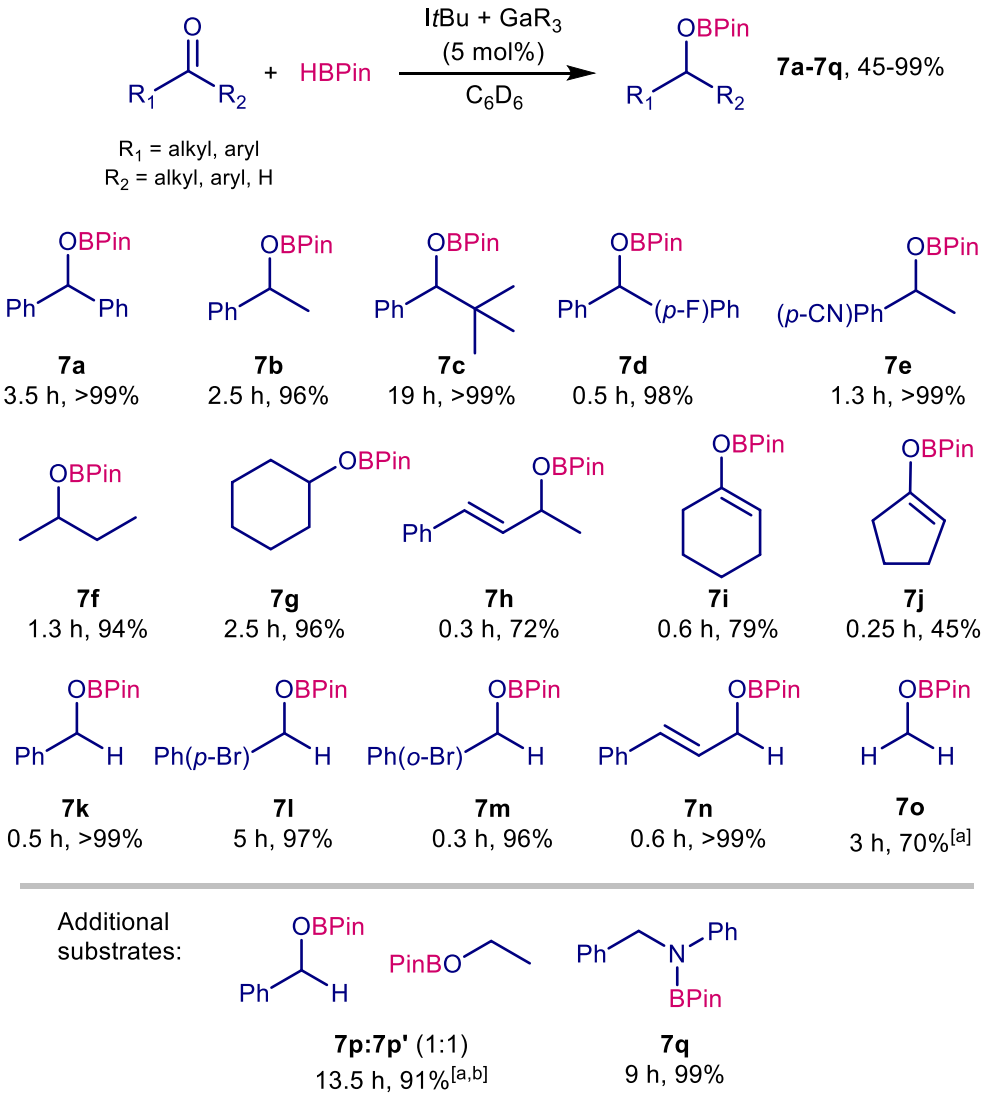


Figure 4 Scope and limitations of I*t*Bu/GaR$_3$ catalyzed hydroboration. Reactions performed in J. Young's NMR tube at 1 mmol scale in 0.5 mL C_6D_6 and yields were calculated against 10 mol% C_6Me_6 internal standard. [a] Reaction performed at 70°C [b] 2 equiv. of HBPin employed

Although catalytic hydroboration through an FLP approach has been investigated in previous cases,[21,22] the unsaturated molecules involved so far have been imines and alkynes. The various aldehydes and ketones discussed here show the diversity which this I*t*Bu/GaR$_3$ system can offer, whilst exhibiting high functional group tolerance and good chemoselectivity. Despite the varied carbonyl-based scope accessible, the system was found to be inactive towards alkenes and alkynes.

Appreciating that borenium gallate (**2**) could potentially be involved during the catalytic cycle, the presence of a metal-hydride fragment within this species prompted us to consider that a classical σ-bond metathesis route could be in operation, led through an initial addition of the substrate across the $\{Ga\text{-}H\}^-$ bond and then generation of the product is triggered by reaction of HBPin across the alkoxide intermediate. However, it must also be acknowledged that the counter cation of **2**, $\{I\textit{t}Bu\text{-}BPin\}^+$, could not be assumed as completely innocent, given the literature precedence for Lewis base-stabilized borenium cations to catalyze hydroboration and hydrosilylation reactions.[21,41] We had to consider that (i) if $BPin^+$ could dissociate from I*t*Bu, a catalytically-viable borenium cation would be liberated in solution, also capable of turnover and (ii) $\{I\textit{t}Bu\text{-}BPin\}^+$ could be responsible for quenching a gallium-alkoxide intermediate and lead to boronate ester product, rather than remaining as a spectator ion. Appreciating the complexity of the three-component system (GaR_3, I*t*Bu and HBpin) under study, we elected to conduct a series of control reactions and kinetic investigations, in order to deduce a potential catalytic pathway and gain an increased understanding of the transformation of hand.

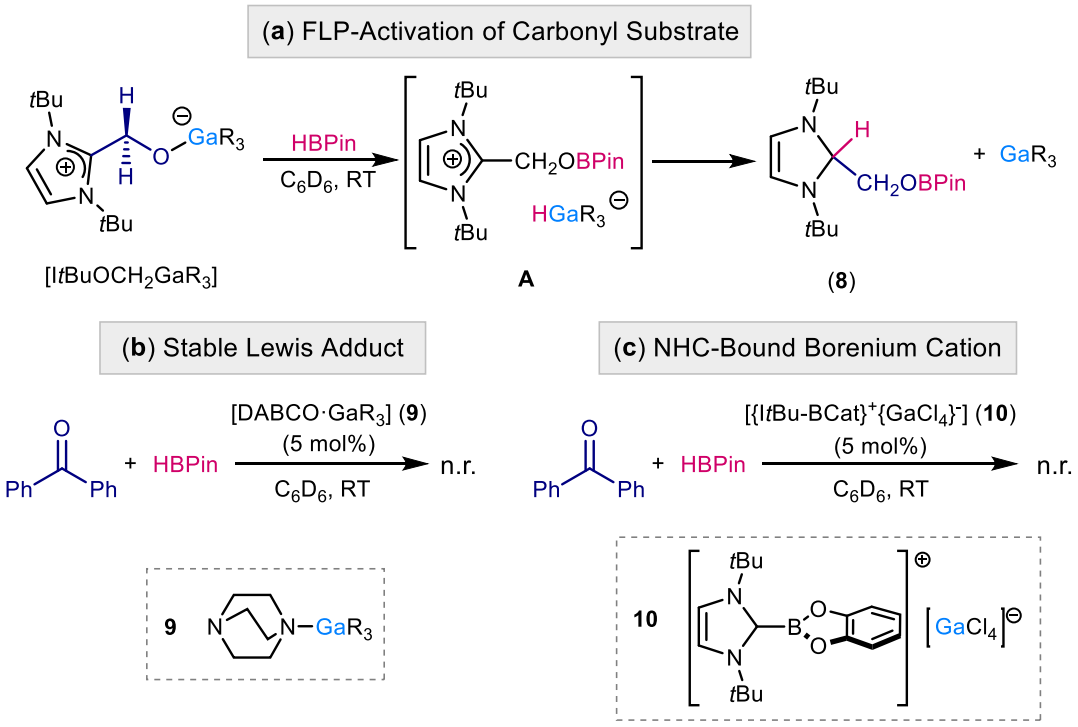
Mechanistic Studies

The optimization stage of this study confirmed that the presence of both I*t*Bu and GaR_3 was key to achieving efficient reactivity, lending further suggestion that FLP-reactivity is likely occurring at some stage within the hydroboration process. Acknowledging that unsaturated substrates such aldehydes and ketones can undergo insertion between I*t*Bu and GaR_3, we first considered the possibility that rather than initial FLP-splitting of HBPin, a converse scenario involving activation of the carbonyl substrate could instead be occurring. In order to test this hypothesis, zwitterionic [$I\textit{t}BuCH_2OGaR_3$] was prepared (by reacting equimolar amounts of formaldehyde, I*t*Bu and

GaR_3),[8] and reacted with one equivalent of HBPin in C_6D_6 (Scheme 4a). Monitoring the reaction by ^{11}B NMR spectroscopy revealed the conversion of the characteristic doublet attributable to HBPin (δ 28.5 ppm) into a broad singlet at δ 22.5 ppm, consistent with the formation of a B-O bond. Analysis of the ^{1}H NMR revealed the quantitative formation of boronic ester (**8**) instead of the 1,2-addition product **7o**. The ^{1}H NMR spectra of this reaction mixture showed an informative triplet at δ 4.47 ppm for the CH fragment in **8** formed by the reduction of the original C2 position of the imidazolydene ring in [I*t*BuCH_2OGaR_3] whereas the protons of the unsaturated backbone resonate at δ 5.37 ppm (Figure SX in ESI). Along with **8**, the presence of free GaR_3 was also observed. Formation of **8** can be rationalized considering the initial σ-bond metathesis of the O-Ga bond in [I*t*BuCH_2OGaR_3] by HBPin to give a putative imidazolium gallate hydride **A** (Scheme 3a) which evolves in a similar way to that describe in 4, via hydride addition to the C2 position of the imidazolium ring to form **8**. These findings suggest that pre-activation of carbonyl-containing substrates by the ItBu/GaR_3 seems unlikely to be a true step involved within the catalytic hydroboration processes.

In order to glean more information into the role of the Lewis acid, stoichiometric reactivity between GaR_3 and HBPin revealed that after 15 days at room temperature in C_6D_6, GaR_2H is quantitatively formed alongside BPin-R (^{11}B NMR, δ 33.8 ppm). Despite the presence of a metal hydride here, subsequent reactivity with benzophenone was sluggish, mirroring the diminished catalytic activity found when using GaR_3 in the absence of its bulky partner, I*t*Bu (Table 1, entry 2) and supporting the key role of the formation of an anionically activated gallate hydride to favor the hydroboration process. The enhanced reactivity of ate hydride species vs neutral hydride complexes has also been noticed by Mulvey[16c] as well as Thomas and Cowley for the hydroboration of alkynes using a variety of Al pre catalysts such as $AlEt_3$ and $LiAlH_4$.[17b] This poor

reactivity of GaR_3 on its own, contrast to the proficiency of the Lewis acid $B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_3$ towards the hydroboration of alkenes as reported by Oestreich,[19,42] where redistribution between the tris(aryl)borane and HBPin promotes the formation of catalytically-active, electron deficient hydroboranes in solution. However, the authors comment that subtle characteristics of the Lewis acid can greatly affect overall reactivity, where $B(C_6F_5)_3$ was found to be catalytically incompetent under the same conditions.



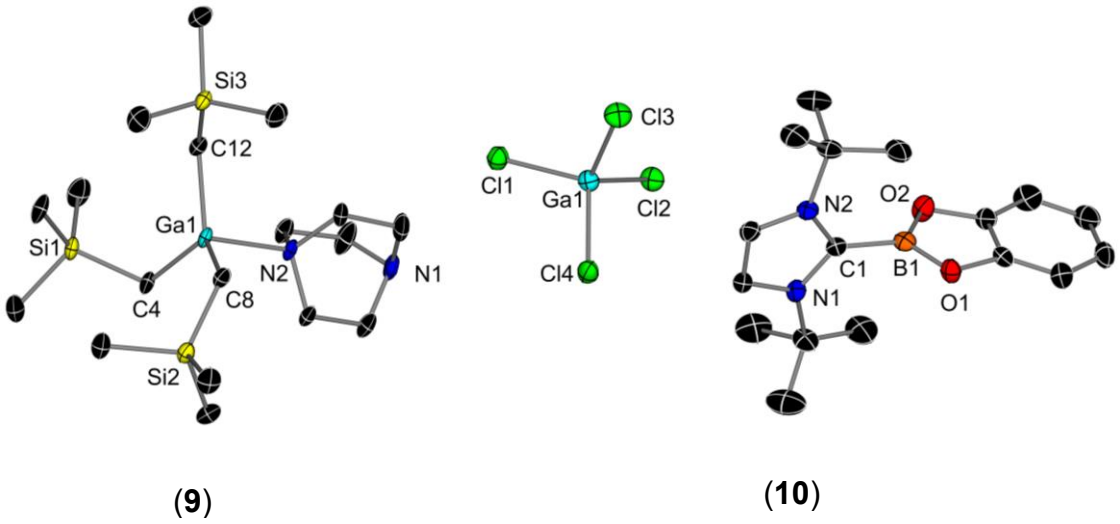
Scheme 4 Control reactions (a) Synthesis of **8** from reaction between [ItBuOCH₂GaR₃] and HBPin (b) Hydroboration of benzophenone using **9** as a catalyst (c) Hydroboration of benzophenone using **10** as a catalyst.

Attention was then turned onto the cationic fragment of **2,** $\{I\textit{t}Bu\text{-}BPin\}^+$, which could not be assumed to be inert without further study. Crudden and co-workers established that FLP-activation of HBPin led to the ion pair $[\{DABCO\text{-}BPin\}^+\{H\text{-}B(C_6F_5)_3\}^-]$, with kinetic studies disclosing that the borenium cation of this species was the true mediator in the catalytic hydroboration of imines

regardless of the nature of the counter anion, and reliant on the ability of the borenium ion to dissociate from the Lewis base.[21] Given the constitutional similarities between [{DABCO-BPin}$^+${H-B(C_6F_5)$_3$}$^-$] and **2**, it was fitting that we considered a similar cationic-dependence within our system. Taking a similar approach to Crudden and substituting the Lewis base I*t*Bu for DABCO in the reaction with GaR_3 and HBPin, it was found that FLP-reactivity was suppressed and instead the formation of the Lewis adduct [DABCO·GaR_3] (**9**) was favored. Compound **9** exhibits structural parallels to [DABCO·$AlEt_3$] as reported by Cowley,[17a] with the only distinct structural difference being in the bond length between the Lewis base and the metal center, where the Al-N distance is notably shorter than the Ga-N bond of **9** [2.054(4) vs 2.150(2) Å] which highlights the large steric demand of the CH_2SiMe_3 groups. The authors then describe the ability of [DABCO·$AlEt_3$] to mediate hydroboration of alkynes and alkenes by the generation of a reactive Al hydride species. However, in our hands **9** did not exhibit any reactivity with HBPin under stoichiometric conditions, and when its catalytic ability was probed by reacting HBPin and benzophenone, it was found that the relevant hydroboration product **7o** could not be detected at room temperature (Scheme 4b) with a modest yield of 23% only reachable when harsher reaction conditions were employed (70°C, 16 h) (see Figure SX in ESI).[37]

Altering our approach, we elected to introduce Cl-BCat to equimolar amounts of I*t*Bu and $GaCl_3$ in hexane at room temperature, which allowed for cleavage of the boron-chlorine bond to result in [{I*t*Bu-BCat}$^+${$GaCl_4$}$^-$] (**10**) which contains a similar cation to that found in **2**. Crystallographic features show that the {$GaCl_4$}$^-$ anion is in a near ideal tetrahedral geometry with an average bond angle of 109.46° and Ga-Cl bond lengths ranging from 2.169(2) to 2.180(2) Å which are typical for this specific anion.[43] Within the cationic component, {I*t*Bu-BCat}$^+$, the C(1)-B(1) bond length of 1.569(11) Å is similar to those detected previously for compounds **2** and **4** (C(25)-B(1) 1.588

(5) Å (**2**), C(4)-B(1) 1.563(4) Å (**4**)), and in good agreement with a related compound reported by Vidović comprised of this same cation balanced by a $\{B(3,5\text{-}Cl_2\text{-}C_6H_3)_4\}^-$ anion and previously discussed herein.[25] Multinuclear NMR data for **10** is also consistent with that reported by Vidović. Additionally, the geometry at boron was found to be in a distorted trigonal planar environment with the sum of the its internal angles being 359° and no evidence of any interactions between the boron center and the $\{GaCl_4\}^-$ anion.



(**9**) (**10**)

Figure 5 Molecular structures of [DABCO·GaR_3] (**9**) and [{I*t*Bu-BCat}$^+${$GaCl_4$}$^-$] (**10**) with displacement ellipsoids at 50% probability for **9** and 30% probability in **10**. All hydrogen atoms have been omitted for clarity. Selected bond angles (°) and lengths (Å) of **9**: C(12)-Ga(1)-N(2) 100.12(9), C(4)-Ga(1)-N(2) 101.85(9), C(8)-Ga(1)-N(2) 101.80(9), N(2)-Ga(1) 2.150(2). Selected bond angles (°) and lengths (Å) of **10**: N(2)-C(1)-B(1) 127.7(7), B(1)-C(1)-N(2) 125.7(7), C(1)-B(1) 1.569(11).

With a suitable cation in hand, **10** was then used to shed light on the potential role of the cationic moiety within the catalysis. Spectroscopic investigations between **10** and a 20-fold excess of benzophenone showed the appearance of a new set of benzophenone resonances in the ^{1}H NMR and the appearance of a new NHC-environment, hinting that a minor degree of displacement of NHC-coordination in favor of the ketone may indeed be possible. This can be rationalized by the

substantial Lewis acidity present at the boron center which is a known characteristic feature of borenium cations.[44] The oxophilicity of borenium cations has also been demonstrated by Ingleson, given the propensity for the Lewis acidity of $\{Et_3N\text{-}BCat\}^+$ species to be assessed via the Gutmann-Beckett method, employing $Et_3P{=}O$ as the reference reagent.[45] Introducing one equivalent of HBPin to benzophenone and 5 mol% **10** displayed no onward reactivity, suggesting the need for a hydridic anion to also be present in order for hydroboration to occur (Scheme 4c).

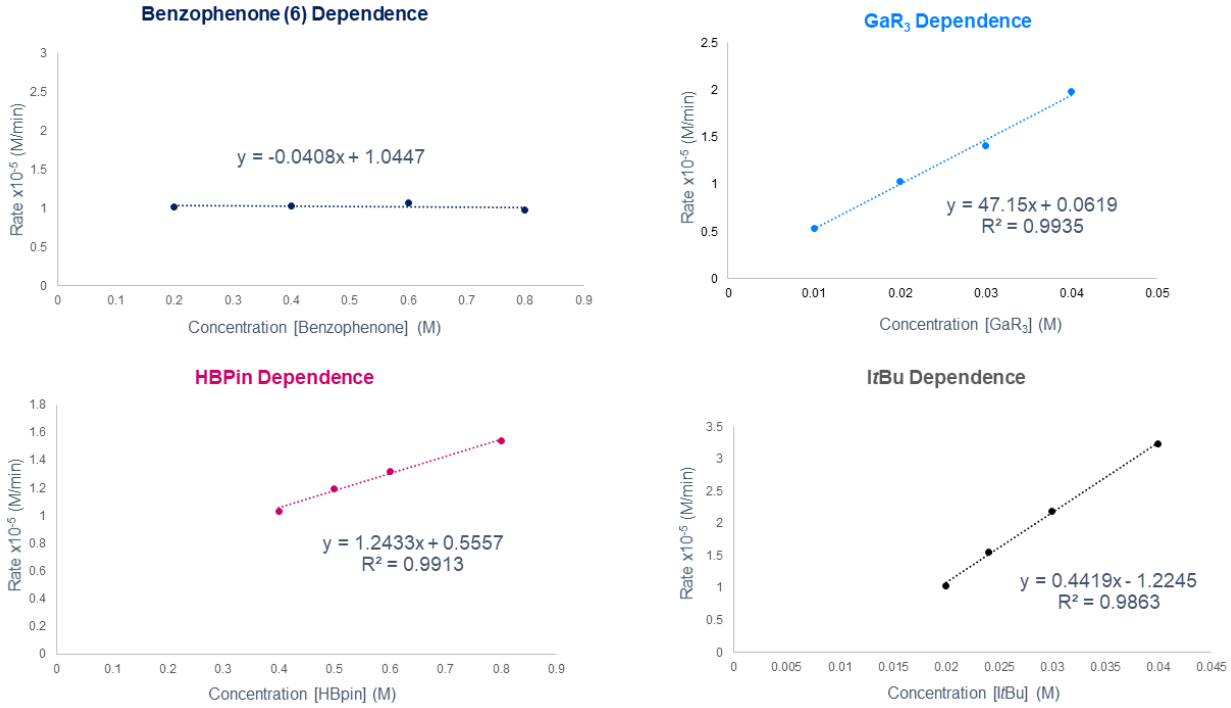


Figure 6 Kinetic profiles of initial rates determination of catalysis components. Results show first order dependence in GaR_3, HBPin and I*t*Bu with a zeroth order dependence detected in **6**.

The results thus far highlight that not only are I*t*Bu and GaR_3 both essential for reactivity, but that pathways based exclusively on the borenium cation can be ruled out. Further details were gathered by kinetic analyses under reaction conditions similar to those employed in the catalytic procedure. ^{1}H NMR monitoring of the reduction of benzophenone (**6**) with HBPin mediated by 5 mol% of

each I*t*Bu and GaR_3 revealed an overall first order decay. In agreement with this, initial rates methods showed a first order dependence in each HBPin, GaR_3 and I*t*Bu, with a zeroth order behavior detected in **6**. It is worth noting that an observed first order dependence on GaR_3 is in line with our initial hypothesis that the inclusion of a second entity of GaR_3 within the anionic fragment of **2**, is most likely a feature of the solid-state constitution of this species. In fact, one could expect that a possible monoanionic $\{GaR_3H\}^-$ species, containing a terminal hydride, will be significantly more nucleophilic that the anion found in **2.**

On the basis of these observations, we can tentatively propose the catalytic cycle shown in Figure 7. Facilitated by the FLP-activating properties of the I*t*Bu/GaR_3 combination towards HBPin, the first step is likely to involve cleavage of the B-H bond of the hydroborane and give rise to **Int I** – akin to $[\{I tBu\text{-}BPin\}^+\{GaR_3(\mu\text{-}H)GaR_3\}^-]$ (**2**). This can be considered as the rate determining step of the reaction in view of the first order dependence established for each of these species from initial rates measurements. Absence of a detectable induction period with our kinetic analyses indicates that cleavage of HBPin is an on-cycle event. The inability to study the solution behavior of **2** lends weight to fact that this borenium/hydride ion pair is highly reactive. While we cannot ascertain from our experiments the definite abilities of the cation, our results imply that partial dissociation of $BPin^+$ from I*t*Bu can occur in the presence of an excess of a carbonyl-containing substrate. This would allow for transformation between short-lived **Int I** into **Int II**, leading to borenium-activation of the carbonyl and facilitating hydride transfer from $\{GaR_3\text{-}H\}^-$, releasing the target product and regeneration of the pre-catalysts, I*t*Bu and GaR_3. Similar pathways involving pre-activation of substrates prior to reduction have shown precedence within catalytic hydrosilylation[41] reactions and in FLP-catalyzed hydrogenation of imines.[46]

Appreciating that formation of **Int II** would likely be driven by the oxophilicity of boron, it is fitting to also acknowledge that $\{I$*t*Bu-BPin$\}^+$ could assume the role of an in-situ quenching agent towards a Ga-alkoxide anion, succeeding insertion of the ketone across the Ga-H bond of **Int I** (see Fig SX in ESI) This pathway would be reminiscent of a typical σ-bond metathesis mechanism known for main group hydrides. Employing **10** as a cationic surrogate to compound **2** and reacting with the anionic alkoxide, LiOEt, indicates a significant degree of oxophilicity of the cation due to the formation of EtO-BCat by multinuclear NMR in D_8-THF.[37] Despite this, the inability to isolate ion pair **2** and test its true behavior towards the reactivity of benzophenone or its potential as an active catalyst, casts speculation on this route.

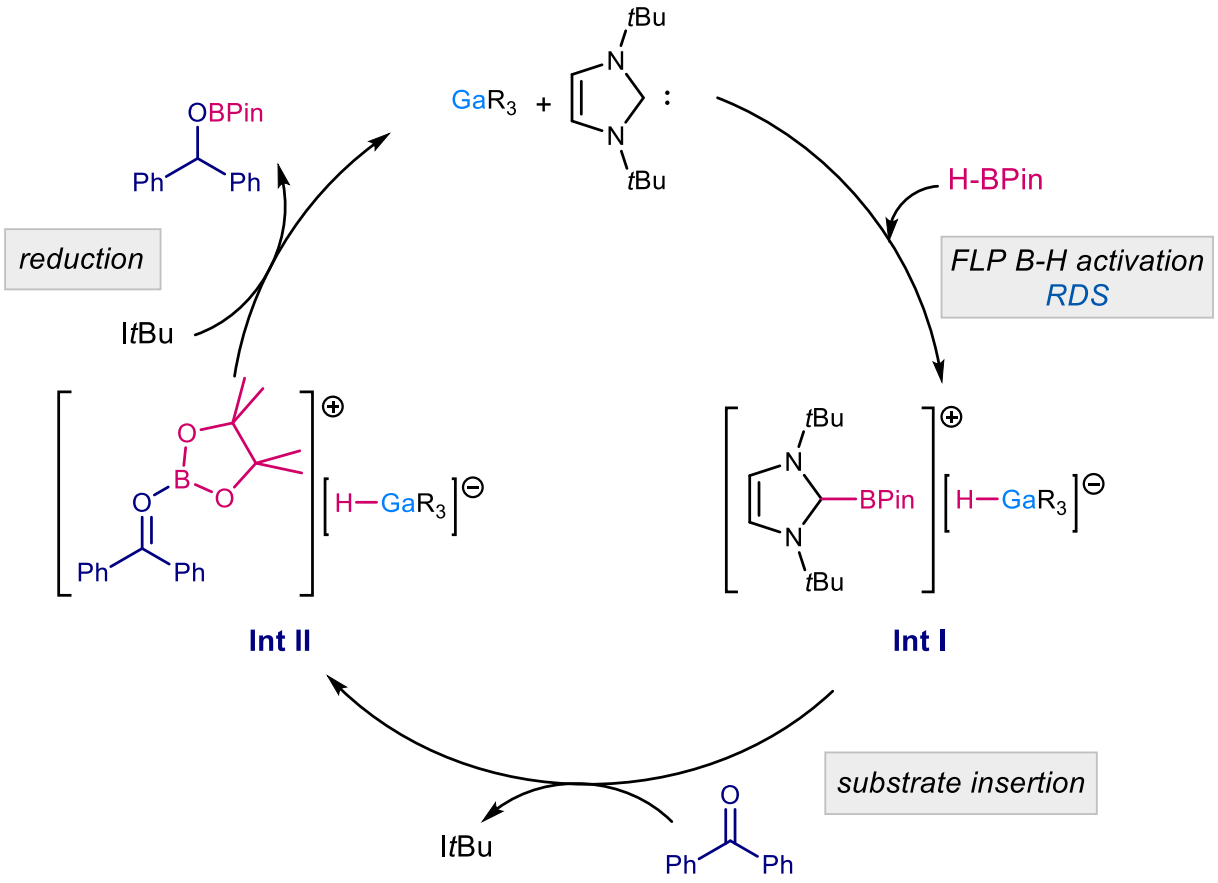


Figure 7 Proposed catalytic cycle for FLP-mediated hydroboration of unsaturated substrates. R = CH_2SiMe_3

In an effort to explore all potential avenues that could be involved, closing control reactions within this study focused on employing BH_3·THF as a catalyst. Previous studies into the nucleophilic decomposition of hydroboranes have revealed that the unexpected presence of BH_3 or hydridoboranes, BH_4^- and $B_2H_7^-$, can often be "Trojan horses" within catalytic hydroboration reactions, and be more realistic mediators of the transformation.[15,47] However, it was found that hydroboration of **6** with HBPin in the presence of 5 mol % BH_3·THF did not proceed under our optimized conditions, or even after heating at 70 °C for 1 h (see Table S1 and Figure SX in ESI).[36] Within the system at hand, it is therefore unlikely that BH_3 or a related hydridoboranes are performing any competing catalytic pathways.

Conclusions

In conclusion, we have uncovered the FLP-capabilities of I*t*Bu/GaR_3 (R = CH_2SiMe_3) by activation of commodity hydroborating reagent, HBPin, and reported the first catalytic applications of this LB/LA combination for the efficient hydroboration of aldehydes and ketones. Initial stoichiometric studies led to the isolation and structural authentication of reactive ion pair [{I*t*Bu-BPin}$^+${GaR_3(μ-H)GaR_3}$^-$] (**2**) resulting from FLP splitting of the B-H bond of the borane. An unprecedented reactivity of the abnormal carbene complex [*a*I*t*Bu·GaR_3] (**1**) with HBPin at elevated temperatures was also unveiled, resulting in the isolation of structural isomer of **2**, [{*a*I*t*Bu-BPin}$^+${GaR_3(μ-H)GaR_3}$^-$] (**4**). Compounds **2** and **4** showed to be highly reactive in solutions evolving at room temperature into Ga abnormal carbene **3** and dihydroimidazole **5** respectively. Upgrading the reactivities of this LB/LA pairing to catalytic conditions allowed for successful hydroboration of a range of carbonyl substrates under mild reaction conditions. Thorough mechanistic studies, including kinetic investigations, suggest that ion pair [{I*t*Bu-

BPin}$^{+}${GaR_3-H}$^{-}$] **Int I** is the active species of this process. Coordination and activation of the substrate to the borenium cation of this pair has been proposed to occur, inscreasing electrophilicity of the C=O bond, prompting subsequent reduction by the {GaR_3-H}$^{-}$ fragment to yield the final product. Despite existing precedence for catalytic applications of FLP-splitting of hydroboranes, the catalytic pathways involved appear to be unique to the Lewis acid/base pairing used, prompting our in depth control reactions and kinetic measurements. While borenium cations in general are known to be excellent promotors within various catalytic transformations, this study demonstrates the importance of the hydridic nature of the anion, and its instrumental role in catalytic turnover.

Experimental Section

All procedures were conducted using standard Schlenk line and glove box techniques under an inert atmosphere of argon. Solvents (pentane, hexane, toluene and Et_2O) were degassed, purified and collected via an MBraun SPS 5 and stored over 4 Å molecular sieves for at least 24 hours prior to use. THF was dried by heating to reflux over sodium-wire/benzophenone ketyl radical and stored over 4 Å molecular sieves for 24 hours prior to use. Deuterated solvents (C_6D_6, D_8-THF and D_8-Tol) were purchased from VWR, dried over NaK alloy for 16 hours and then cycled through three rounds of degassing by employing a freeze-pump-thaw method. The deuterated solvents were then collected via vacuum transfer and stored argon atmosphere over 4 Å molecular sieves. Pinacolborane was purchased from Fluorochem, stored in an argon-sealed ampule and cycled through three rounds degassing by employing a freeze-pump-thaw method. Substrates **4a-q** were purchased from Sigma-Aldrich, Fluorochem or Alfa-Aesar – liquids were stored over 4 Å molecular sieves for 24 h prior to use. DABCO and phenol were purchased from Sigma Aldrich, sublimed before use and stored in a glovebox under Ar atmosphere. NMR spectra were recorded

on Bruker spectrometers operating at either 300 or 400 MHz. ^{1}H NMR spectra: 300.1 or 400.1 MHz, ^{13}C{^{1}H} NMR spectra: 75.5 or 100.6 MHz, ^{19}F NMR spectra: 282.4 MHz. $Ga(CH_2SiMe_3)_3$,[48] I*t*Bu[49] *a*I*t*Bu·GaR_3 (**1**)[23] were prepared according to literature methods.

Synthesis of [{I*t*Bu-BPin}$^{+}${GaR_3(μ-H)GaR_3}$^{-}$] (R = CH_2SiMe_3) (2)

To an argon-prepared Schlenk flask, 1 mmol (0.33 g) of GaR_3 was dissolved in 5 mL of pentane and the resulting solution was cooled to 0 ºC, followed by the addition of 1 mmol (0.15 mL) of HBPin. Then, an equimolar amount of I*t*Bu (1 mmol, 0.180 g) was added and a fine, white suspension was obtained. This mixture was stirred at 0 ºC for 1 h, resulting in a colourless solution which was then concentrated *in vacuo*, to approx. 1 mL of solvent. Cooling to -30 ºC afforded a crop of colourless crystals, determined as **2** by X-ray diffraction. Repeated attempts at the isolation of **2** for analyses beyond x-ray diffraction led to the inevitable formation of an abnormal NHC-Ga complex, [BPin{[N(*t*Bu)]$_2$CHCGa(R)$_3$}] (**3**), which co-crystallizes alongside GaR_3 and *a*I*t*Bu·GaR_3. Yield = 110 mg, 17% (MW = 637.63). Anal. calcd. for $C_{29}H_{64}BGaN_2O_2Si_3$: C, 54.45; H, 10.40; N, 4.38. Found: C, 53.59; H, 10.64; N, 4.70.

^{1}H NMR (298 K, C_6D_6): δ / ppm = 7.32 (s, 1H, imidazole backbone), 1.64 (s, 9H, *t*Bu), 1.26 (s, 9H, *t*Bu), 1.01 (s, 12H, C*H*$_3$, BPin), 0.33 (s, 27H, C*H*$_3$, R), -0.22 (s, 6 H, C*H*$_2$, R). ^{11}B NMR (298 K, C_6D_6): δ / ppm = 28.63 (C(2)-BPin) ^{13}C NMR (298 K, C_6D_6): δ / ppm = 160.3 (N*C*(BPin)N), 129.1 (*C*H, imidazole backbone), 86.2 (C_q, BPin), 61.2 (*C*(CH$_3$)$_3$), 58.7 (*C*(CH$_3$)$_3$), 31.9 (*C*H$_3$, *t*Bu), 30.7 (*C*H$_3$, *t*Bu), 25.6 (*C*H$_3$, BPin), 3.8 (*C*H$_3$, R), 2.6 (*C*H$_2$, R).

Synthesis of [{*a*I*t*Bu-BPin}$^{+}${GaR_3(μ-H)GaR_3}$^{-}$] (R = CH_2SiMe_3) (4)

1 mmol (0.513 g) of *a*I*t*Bu·GaR_3 was dissolved in 5 mL of hexane followed by the addition of 1 mmol (0.15 mL) of HBPin. This mixture was heated to reflux for 4 h, resulting in a colourless

solution. This solution was then concentrated *in vacuo*, to approx. 1 mL of solvent. Cooling to -30 ^{o}C afforded a crop of colourless crystals, determined as **4** by X-ray diffraction. Repeated attempts at the isolation of **3** for analyses beyond x-ray diffraction led to reduction of the cationic fragment to give, [H_2{[N(*t*Bu)]$_2$CHCBPin}] (**5**). Yield = 83 mg, 27% (MW = 308.27). Anal. calcd. for $C_{17}H_{33}BN_2O_2$: C, 66.24; H, 10.79; N, 9.09 Found: C, 64.48; H, 10.69; N, 8.66.

^{1}H NMR (298 K, C_6D_6): δ / ppm = 6.92 (s, 1H, imidazole backbone), 4.43 (s, 2H, C(2)-*H*$_2$), 1.35 (s, 9H, *t*Bu), 1.12 (s, 12H, C*H*$_3$, BPin), 0.86 (s, 9H, *t*Bu). ^{11}B NMR (298 K, C_6D_6): δ / ppm = 29.0 (C(4)-*B*) ^{13}C NMR (298 K, C_6D_6): δ / ppm = 140.6 (N*C*(BPin)N), 129.1 (*C*H, imidazole backbone), 82.4 (*C*$_q$, BPin), 68.2 (*C*(2)-H$_2$), 55.6 (*C*(CH$_3$)$_3$), 51.8 (*C*(CH$_3$)$_3$), 31.9 (residual hex.), 27.9 (*C*H$_3$, *t*Bu), 27.5 (*C*H$_3$, *t*Bu), 24.8 (*C*H$_3$, BPin), 23.0 (residual hex.), 14.3 (residual hex.).

Synthesis of [DABCO·GaR$_3$] (R = CH$_2$SiMe$_3$) (9)

In a Schlenk flask, 1 mmol (0.33 g) of GaR$_3$ was dissolved in 10 mL of hexane under argon atmosphere followed by the addition of 1 mmol (0.15 mL) of HBPin. To this, an equimolar amount of DABCO (1 mmol, 0.112 g) was added resulting in a colourless solution. The mixture was allowed to stir at room temperature for three hours and then concentrated under reduced pressure to give a white suspension. Applying gentle heating regained a colourless solution which, upon slow cooling to room temperature, resulted in a crop of colourless crystals. Measurement by X-Ray diffraction revealed the product to be Lewis adduct [DABCO·GaR$_3$] (**9**). Yield: 0.222 g, 50% (MW = 443.55). Anal. Calcd. for $C_{18}H_{45}GaN_2Si_3$: C, 48.74; H, 10.23; N, 6.32. Found: C, 48.14; H, 10.27; N, 6.47. **^{1}H NMR (298 K, C_6D_6)** δ / ppm = 2.24 (s, 12H, C*H*$_2$, DABCO), 0.30 (s, 27H, C*H*$_3$, R), -0.61 (s, 6H, C*H*$_2$, R). **^{13}C{^{1}H} NMR (298 K, C_6D_6)** δ / ppm = 45.9 (*C*H$_2$, DABCO), 3.2 (*C*H$_3$, R), 0.3 (*C*H$_2$, R).

Synthesis of [{I*t*Bu-BCat}$^+${$GaCl_4$}$^-$] (10)

In an argon-prepared Schlenk flask, 1 mmol (0.176 g) of $GaCl_3$was dissolved in 10 mL of hexane followed by the addition of 1 mmol (0.154 g) of Cl-BCat[50] giving a colourless solution. Addition of an equimolar amount of I*t*Bu (0.180 g) gave a white suspension which was allowed to stir at room temperature for 5 hours. Removal of all volatiles under reduced pressure have a white solid which was then re-dissolved in 5 mL of toluene and applying gentle heating – a colourless solution and a small amount of orange oil were obtained. Slow cooling to room temperature produced a crop of colourless crystals which were determined to be [{I*t*Bu-BCat}$^+${$GaCl_4$}$^-$] (**10**). Yield: 0.314 g, 61% (MW = 510.72). Anal. Calcd. for $Cl_4GaC_{17}H_{24}BN_2O_2$: C, 39.98; H, 4.74; N, 5.49. Found: C, 38.72. H; 4.77; N, 5.68. **^{1}H NMR (298 K, C_6D_6/D_8-THF)** δ / ppm = 7.54 (s, 2H, C*H*, imidazole backbone), 7.28 (m, 2H, C_{Ar}-*H*), 7.07 (m, 2H, C_{Ar}-*H*), 1.27 (s, 18H, CH_2, *t*Bu). **^{11}B NMR (298 K, C_6D_6/D_8-THF)** δ / ppm = 27.8 (br. s, {I*t*Bu-*B*Cat}$^+$). **^{13}C{^{1}H} NMR (298 K, C_6D_6/D_8-THF)** δ / ppm = 146.8 (C-*B*Cat), 125.6 (C_{Ar}-H), 123.4 (*C*-H, imidazole backbone), 120.8 (C_q), 114.3 (C_{Ar}-H), 62.6 (*C*(CH_3)$_3$), 30.2 (C(*C*H_3)$_3$).

General Catalytic Procedure

Reactions were performed in a J. Young's NMR tube at 2.0 M in C_6D_6 with 1 mmol of substrate and 1.05 mmol (0.15 mL) of HBPin. 0.05 mmol (9 mg, 5 mol %) of I^{t}Bu and 0.05 mmol (17 mg, 5 mol %) of GaR_3 (or the relevant catalyst according to **optimization table**) were added and the reactions monitored by multinuclear NMR spectroscopy until evolution ceased.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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