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# Two-Coordinate NHC-Supported Zn<sup>II</sup> Organocations: Steric and Electronic Tunability and Use in Alkyne Hydroboration Catalysis

Refka Guerhazi,<sup>[a]</sup> David Specklin,<sup>[a]</sup> Christophe Gourlaouen,<sup>[a]</sup> Pierre de Frémont,<sup>[a]</sup> and Samuel Dagorne\*<sup>[a]</sup>

Dedicated to Professor Rinaldo Poli on the occasion of his 65th birthday.

We herein report on the synthesis, structure, and use in alkyne hydroboration catalysis of [(IPrCl)Zn–R]<sup>+</sup> and [(tBu)Zn–R]<sup>+</sup> cations bearing IPrCl (IPrCl = 1,3-bis[2,6-bis(1-methylethyl)phenyl]-4,5-dichloro-1,3-dihydro-imidazol-2-ylidene) and the sterically demanding tBu carbene (tBu = 1,3-bis(1,1-dimethylethyl)-1,3-dihydro-imidazol-2-ylidene). Ionization of neutral precursors [(IPrCl)ZnR<sub>2</sub>] (1 a, R=Et; 1 b, R=Me) and [(tBu)ZnEt<sub>2</sub>] (2) with one equivalent of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] led to with robust and stable two-coordinate Zn<sup>II</sup> cations [(IPrCl)Zn–R]<sup>+</sup> (3 a, R=Et; 3 b, R=Me) and [(tBu)Zn–Et]<sup>+</sup> (4), respectively, all isolated as [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup> salts. Further derivatization of alkyl cations 3 b and 4 by reaction with one equivalent of [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] afforded cations [(IPrCl)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> (5) and [(tBu)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> (6) as [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup> salts,

with cation 6 displaying a limited stability in solution. The molecular structures of cations 3 b, 4 and 5 were confirmed through X-ray diffraction studies. Among stable cations, Fluoride ion affinity (FIA) estimations agree with cation 5 being the most Lewis acidic in thus far reported [(IPrCl)Zn–R]<sup>+</sup> cations. In the presence of pinacol borane and 1-octyne, cations 3 a–b, 5 and [(IPrCl)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> (5 mol%) slowly catalyze the selective *cis*-hydroboration of 1-octyne to the vinylborane product A. Cation 5 also mediates 2-hexyne hydroboration to afford a mixture of hydroboration products B and C. In the case of hydroboration catalysis mediated by cations 5 and [(IPrCl)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup>, experimental data and preliminary DFT calculations are consistent a Lewis-acid-type catalysis.

## Introduction

Over the past twenty years, metal complexes supported by *N*-heterocyclic carbenes (NHCs) have found widespread use and applications across chemical science, notably in metal-mediated homogeneous catalysis and as sources of novel fundamental reactivity in organometallic chemistry.<sup>[1–4]</sup> The strong  $\sigma$ -donating properties of NHCs combined with their steric tunability usually provide enhanced stability to the resulting M–NHC complexes, which has allowed the characterization of unprecedented reactive metal/heteroelement species.<sup>[5–10]</sup> In particular, NHC-supported Zn<sup>II</sup> complexes currently attracts an increasing attention for use in catalysis given that Zinc is a cheap, low toxicity and earth-abundant metal source.<sup>[11]</sup> Over the past ten years but with significant developments the past five years,

such complexes have been successfully exploited as catalysts for various chemical functionalizations ranging from hydrosilylation of unsaturated substrates (primarily alkenes, alkynes, nitriles and CO<sub>2</sub>), allylic alkylation, alkyne dehydroboration/diboration, C–H borylation of heteroarenes to polymerization catalysis of polar monomers.<sup>[12]</sup>

Well-defined Zn(II) organocations have long been of interest because the enhanced Lewis acidity at Zn(II) may lead to stronger electrophiles able to activate various substrates in an effective (and possibly catalytic) manner.<sup>[13]</sup> In this regard, low-coordinate Zn(II) cations (three-coordinate and below) are particular interesting targets since they combine low coordination and a cationic Zn(II) center. In the area, we earlier reported that two-coordinate Zn(II) organocations of the type [(NHC)Zn–R]<sup>+</sup> (R = alkyl, aryl) are viable and stable electrophiles thanks to NHC stabilization.<sup>[12d]</sup> Such cations were initially shown to be effective alkene, alkyne and CO<sub>2</sub> hydrosilylation. More recently, Gandon and coll. successfully used the cation [(IPr)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> as a  $\pi$ -Lewis acid for alkynylcycloheptatrienes rearrangement, hydroarylation and transfer hydrogenation catalysis,<sup>[14]</sup> while Ingleson and coll. demonstrated that cation [(IPr)Zn–Et]<sup>+</sup> may be used as pre-catalyst for the C–H borylation of heteroarenes.<sup>[12a]</sup> Thus far, known stable cations [(NHC)Zn–R]<sup>+</sup> only incorporate IPr as a carbene source: as a comparison, two-coordinate Zn(II) cations stabilized with the less sterically hindered IMes carbene are not thermally stable.<sup>[12d]</sup> To further develop these electrophiles and probe the electronic/steric suitability of various NHCs for such compounds, we herein report the synthesis and structural characterization of

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Part of the “celebratory collection for Rinaldo Poli”.

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novel  $[(\text{NHC})\text{Zn-R}]^+$  cations bearing  $\text{IPrCl}$  ( $\text{IPrCl} = 1,3\text{-bis}[2,6\text{-bis}(1\text{-methylethyl})\text{phenyl}]\text{-4,5-dichloro-1,3-dihydro-imidazol-2-ylidene}$ ), a less  $\sigma$ -donating NHC (*vs.*  $\text{IPr}$ ), and the sterically demanding  $\text{ItBu}$  carbene ( $\text{ItBu} = 1,3\text{-bis}(1,1\text{-dimethylethyl})\text{-1,3-dihydro-imidazol-2-ylidene}$ ).<sup>[15]</sup> Besides, we also first show that these  $[(\text{NHC})\text{Zn-R}]^+$  cations may mediate alkyne hydroboration catalysis at room temperature to afford the corresponding vinylborane products.

## Results and Discussion

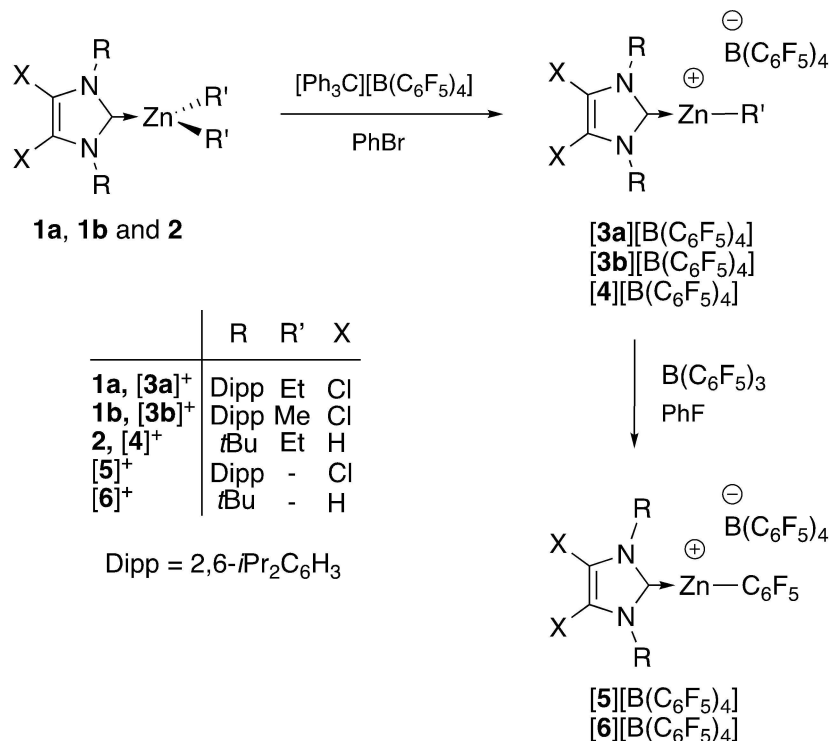
### Synthesis of the neutral NHC–Zn adduct precursors

The synthesis and characterization of the corresponding neutral precursors  $[(\text{IPrCl})\text{ZnR}_2]$  (**1a**,  $\text{R}=\text{Et}$ ; **1b**,  $\text{R}=\text{Me}$ ) and  $[(\text{ItBu})\text{ZnEt}_2]$  (**2**) was performed before subsequent ionization. Adducts **1a**, **1b** and **2** (Scheme 1) were prepared by addition of  $\text{ZnR}_2$  ( $\text{R}=\text{Me}$ ,  $\text{Et}$ ) to 1 equiv. of the corresponding NHC (toluene, room temperature), and isolated in high yields as colorless or pale-yellow solids. The NMR data agree with the effective and quantitative formation of 1/1 NHC/ $\text{ZnR}_2$  adducts. In particular, the presence of a characteristic  $^{13}\text{C}\{^1\text{H}\}$  NMR resonance assigned to the  $\text{Zn-C}_{\text{carbene}}$  moiety ( $\delta = 192.6$ ,  $192.4$  and  $186.0$  ppm for **1a**, **1b** and **2**, respectively) is consistent with adduct formation. These  $\text{Zn-C}_{\text{carbene}}$  chemical shifts are comparable to those reported for related  $[(\text{NHC})\text{ZnR}_2]$  adducts.<sup>[16]</sup> Though no X-ray diffraction (XRD) quality crystals of adducts **1a**, **1b** and **2** could be grown, such adducts are assumed to be monomeric in the solid state and in solution (RT) given their structural (steric and

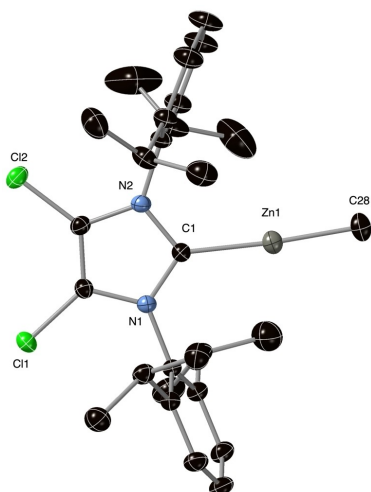
electronic) similarities to reported XRD-characterized  $[(\text{NHC})\text{ZnR}_2]$  monomers.<sup>[17]</sup>

### Synthesis and characterization of NHC–Zn cations

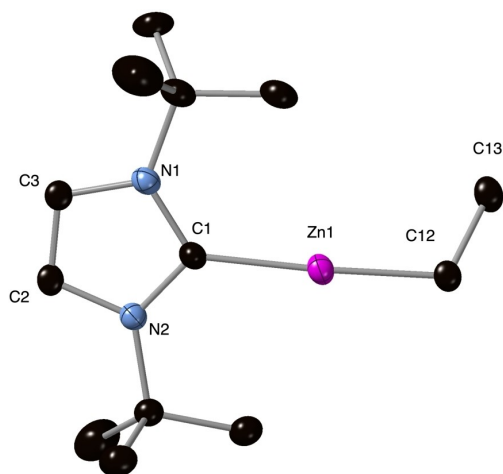
The  $\text{Zn-alkyl}$  cations  $[(\text{IPrCl})\text{Zn-R}]^+$  (**[3a]**<sup>+</sup>,  $\text{R}=\text{Et}$ ; **[3b]**<sup>+</sup>,  $\text{R}=\text{Me}$ ) and  $[(\text{ItBu})\text{ZnEt}]^+$  (**[4]**<sup>+</sup>) were prepared by an alkide abstraction ionization reaction of the corresponding neutral precursors **1a**–**1b** and **2**, respectively, with 1 equiv.  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (Scheme 1). The resulting cations **[3a]**<sup>+</sup>, **[3b]**<sup>+</sup> and **[4]**<sup>+</sup> were all isolated as  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  salts in good yields as off-white solids. Importantly, these three salts are stable in  $\text{CD}_2\text{Cl}_2$  or  $\text{C}_6\text{D}_5\text{Br}$  under inert atmosphere, indicating the suitability of carbenes  $\text{IPrCl}$  and  $\text{ItBu}$  for the stabilization of two-coordinate  $\text{Zn(II)}$  organocations. In the case of **[3b]** $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and **[4]** $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , XRD studies unambiguously confirmed their molecular structures. They crystallize as  $[(\text{IPrCl})\text{Zn-Me}]^+ / [(\text{ItBu})\text{ZnEt}]^+$  and  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  ions with no cation-anion interaction in the solid state. As shown in Figure 1 and Figure 2, cations  $[(\text{IPrCl})\text{Zn-Me}]^+$  and  $[(\text{ItBu})\text{ZnEt}]^+$  both feature a nearly linear two-coordinate  $\text{Zn(II)}$  center ( $\text{C-Zn-C} = 176.1(2)$  and  $173.2(2)$ , respectively) and display very similar bonding parameters. The  $\text{Zn-R}$  bond distances ( $1.911(4)$  and  $1.934 \text{ \AA}$  for **[3b]**<sup>+</sup> and **[4]**<sup>+</sup>, respectively) are a bit shorter than those in related neutral adducts such as  $[(\text{IPr})\text{ZnMe}_2]$  ( $1.99 \text{ \AA}$  average). Also, reflecting a more Lewis acidic and a  $sp$ -hybridized  $\text{Zn(II)}$  center, the  $\text{Zn-NHC}$  bond distances ( $1.958(3)$  and  $1.952(3) \text{ \AA}$  for **[3b]**<sup>+</sup> and **[4]**<sup>+</sup>, respectively) are strikingly shorter than those in  $[(\text{IPr})\text{ZnMe}_2]$  ( $2.112(2) \text{ \AA}$ ),  $[(\text{IPr})\text{Zn}(\text{C}_6\text{F}_5)_2]$  ( $2.034(2) \text{ \AA}$ ) and  $[(\text{ItBu})\text{Zn}(\text{C}_6\text{F}_5)_2]$  ( $2.038(3) \text{ \AA}$ ).<sup>[16]</sup> In solution, all



Scheme 1. Synthesis of cationic NHC–Zn species.



**Figure 1.** Molecular structure (ORTEP view) of cation [(IPrCl)Zn-Me]<sup>+</sup> (**[3b]**<sup>+</sup>) with selected atom labeling. The hydrogen atoms and the anion are omitted for clarity. Selected bond distances (Å) and angles (°): Zn-Me = 1.911(4); Zn-NHC = 1.958(3); C-Zn-C = 176.1(2).



**Figure 2.** Molecular structure (ORTEP view) of cation [(ItBu)Zn-Et]<sup>+</sup> (**[4]**<sup>+</sup>) with selected atom labeling. The hydrogen atoms and the anion are omitted for clarity. Selected bond distances (Å) and angles (°): Zn-Et = 1.934(4); Zn-NHC = 1.952(3); C-Zn-C = 173.2(2).

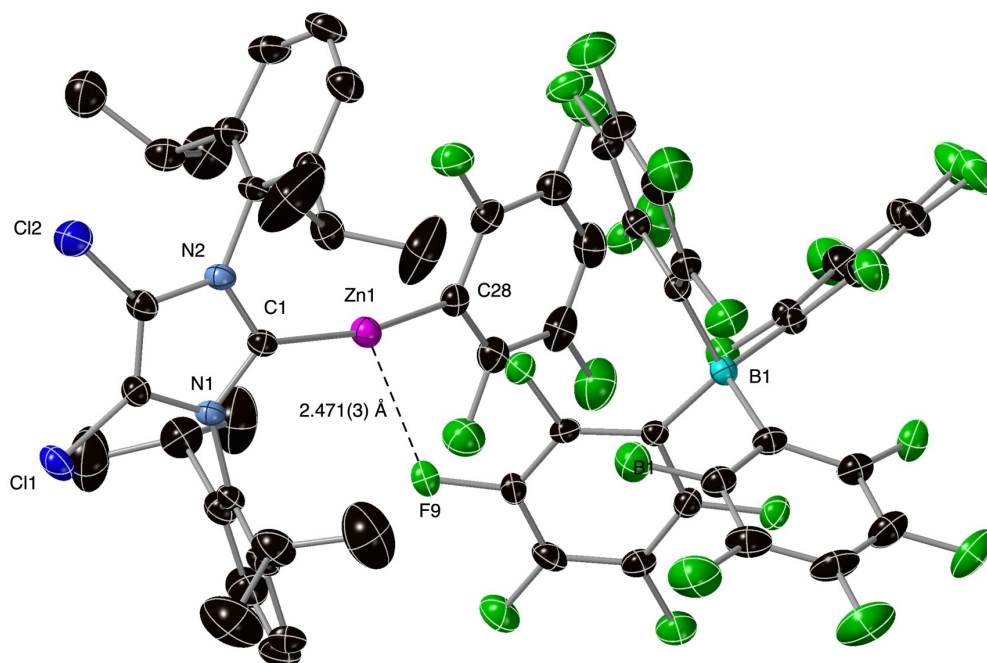
NMR data agree with the proposed formulation and thus the presence of Zn-R<sup>+</sup> and NHC-Zn moieties. In particular and characteristically, the <sup>13</sup>C NMR Zn-C<sub>carbene</sub> chemical shifts for **[3a]**<sup>+</sup> and **[3b]**<sup>+</sup> (δ = 164.4 and 164.2 ppm, respectively) are significantly upfield shifted versus those of the respective neutral precursors (δ = 192.6 and 192.4 ppm), in line with enhanced Lewis acidity at Zn(II) as expected upon going to cationic species. The solution structure was further studied for salt [(IPrCl)Zn-Me][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**[3b]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) through <sup>1</sup>H and <sup>19</sup>F DOSY NMR experiments (CD<sub>2</sub>Cl<sub>2</sub>, RT). For both nuclei, a very similar diffusion coefficient (<sup>1</sup>H: *D* = 7.46 × 10<sup>-10</sup> m<sup>2</sup>/s; <sup>19</sup>F: *D* = 7.34 × 10<sup>-10</sup> m<sup>2</sup>/s) was measured, thus leading to nearly identical estimated hydrodynamic volumes (<sup>1</sup>H: *V*<sub>estimated</sub> = 1270 Å<sup>3</sup>; <sup>19</sup>F: *V* = 1334 Å<sup>3</sup>). The latter is consistent with the [(IPrCl)Zn-Me]<sup>+</sup>

cation and the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> ion remaining in close proximity in solution under the studied conditions, despite the absence of short cation/anion contacts in the solid state structure.

To enhance Lewis acidity at Zn(II), the Zn-C<sub>6</sub>F<sub>5</sub> cationic derivatives [(IPrCl)Zn-C<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**[5]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) and [(ItBu)Zn-C<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**[6]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) were targeted and prepared through an alkyl/C<sub>6</sub>F<sub>5</sub> exchange reaction between **[3b]**<sup>+</sup>/ **[4]**<sup>+</sup> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Salts **[5]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and **[6]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were isolated in high yield as off-white solids. While the IPrCl adduct **[5]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is soluble and stable for days in CD<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>D<sub>5</sub>Br, the ItBu analogue **[6]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] exhibits a poor solubility in the latter solvents but is quite soluble in PhF. Somewhat surprisingly and unlike all cations of the present series, species **[6]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is unstable in solution (CD<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>D<sub>5</sub>Br) to decompose within hours at room temperature to unidentified species, precluding its further use for reactivity studies. In the case of cation **[5]**<sup>+</sup>, its molecular structure was confirmed through XRD studies. As shown in Figure 3, salt **[5]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] crystallizes as [(IPrCl)Zn-C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> and [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> ions in close contact to one another as evidenced by a rather short Zn⋯F distance (2.471(3) Å), lying well-below the sum of the van der Waals radii of the Zn and F atoms (2.86 Å).<sup>[18]</sup> Nevertheless, such distance is too long to be considered as a bonding interaction, as it remains significantly longer than known Zn-F bond distances bonds that range from 1.84–2.03 Å for terminal Zn-F bonds to 2.26 Å in a Zn-F-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> species bearing a bridging fluoride.<sup>[19]</sup> As shown in Figure S33 (SI), the non-covalent interactions (NCI) plot for the Zn⋯F contacts in **[5]**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is consistent with dispersion type interactions between the two atoms.

The Lewis acidity of the prepared Zn<sup>II</sup> cations was evaluated through estimation of their Fluoride Ion Affinity (FIA) by DFT in PhBr medium (B3LYP/6-31+G\*\*, PhBr as solvent through a PCM model), and compared to earlier reported [(IPr)Zn-R]<sup>+</sup> systems and landmark Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[12d]</sup> Consistent with a more electrophilic Zn<sup>II</sup> center due to a less σ-donating NHC ligand (IPrCl vs. IPr), cations [(IPrCl)Zn-R]<sup>+</sup> (R=Me, FIA = 156.5 kJ·mol<sup>-1</sup>; R=C<sub>6</sub>F<sub>5</sub>, FIA = 191.4 kJ·mol<sup>-1</sup>) are more Lewis acidic than [(IPr)Zn-R]<sup>+</sup> cations (R=Me, FIA = 148.3 kJ·mol<sup>-1</sup>; R=C<sub>6</sub>F<sub>5</sub>, FIA = 185.5 kJ·mol<sup>-1</sup>). Expectedly, the FIA of [(ItBu)Zn-Et]<sup>+</sup> (FIA = 154.2 kJ·mol<sup>-1</sup>) is similar to those of the Zn-Me cations **[3b]**<sup>+</sup> and [(IPr)Zn-Me]<sup>+</sup>. Thus, cation **[5]**<sup>+</sup> is the most Lewis acidic stable Zn<sup>II</sup> cation across the [(NHC)Zn-R]<sup>+</sup> series thus far, yet being a weaker Lewis acid (in PhBr) than B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (FIA = 220.5 kJ·mol<sup>-1</sup>).<sup>[20]</sup> Further, the electronic structure and bonding at Zn<sup>II</sup> for cations **[3a]**<sup>+</sup>, **[3b]**<sup>+</sup>, **[4]**<sup>+</sup> and **[5]**<sup>+</sup> was also DFT computed (B3LYP/6-31+G\*\*, Table S1, SI), leading to NBO charges at Zn<sup>II</sup> of 1.25, 1.28, 1.18 and 1.30 for **[3a]**<sup>+</sup>, **[3b]**<sup>+</sup>, **[4]**<sup>+</sup> and **[5]**<sup>+</sup> respectively. The Wiberg indexes (WI) for the Zn-NHC bond (ranging from 0.333 to 0.419) and Zn-X bonds (going from 0.454 to 0.594) are all consistent with polar covalent bonds. The Zn-NHC bond is estimated to be more covalent upon going from alkyl cation **[3b]**<sup>+</sup> to the [Zn-C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> cation **[5]**<sup>+</sup> (WI = 0.348 and 0.386, respectively), possibly reflecting a stronger NHC σ-donation to stabilize the more electrophilic Zn(II) center in **[5]**<sup>+</sup>.





**Figure 3.** Molecular structure of salt [(IPrCl)Zn-C<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with selected atom labeling. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zn-C<sub>6</sub>F<sub>5</sub> = 1.924(3); Zn-NHC = 1.953(3); Zn...F = 2.471(3); C-Zn-C = 167.3(1).

### Alkyne hydroboration catalysis by NHC-Zn cations

Zn-catalyzed functionalization of organic molecules with hydroboranes remain little studied though NHC-supported Zn cations were recently reported to be effective catalysts for alkyne diboration and C-H borylation of heteroarenes, for which the Lewis acidity of the Zn<sup>II</sup> plays an important role for catalytic activity.<sup>[12a,c]</sup> We investigated Lewis acidic cations [3a]<sup>+</sup>, [3b]<sup>+</sup>, [5]<sup>+</sup> and [(IPr)ZnC<sub>6</sub>F<sub>5</sub>]<sup>+</sup> in alkyne hydroboration catalysis. In the presence of pinacol borane (pinBH) and 1-octyne (20 equiv. of each), all these cations catalyze the *cis*-hydroboration of 1-octyne at room temperature to selectively afford the corresponding (*E*)-vinylborane product **A** ( $\beta$  isomer), as deduced

from NMR and GC-MS data (Table 1). The activity correlates with the Lewis acidity of these cations, with the most Lewis acidic catalyst [5]<sup>+</sup> being the most active. Thus, at best, with [5]<sup>+</sup>, hydroboration product **A** formed in 77% NMR yield after 24 h at RT (entry 7, Table 1) while catalysis with all other cations proceeded significantly slower (entries 1, 4 and 9, Table 1), but with cation [(IPr)ZnC<sub>6</sub>F<sub>5</sub>]<sup>+</sup> being more active than less Lewis acidic [3a]<sup>+</sup> and [3b]<sup>+</sup> (entries 1, 4 vs. 9, Table 1). Under these conditions (CD<sub>2</sub>Cl<sub>2</sub>, RT), the more Lewis acidic Zn-C<sub>6</sub>F<sub>5</sub> cations, *i.e.* [5]<sup>+</sup> and [(IPr)ZnC<sub>6</sub>F<sub>5</sub>]<sup>+</sup>, retain their integrity as the catalysis proceeds strongly suggesting a Lewis acid-type catalysis. In contrast, substantial decomposition of the Zn-alkyl cations [3a]<sup>+</sup> and [3b]<sup>+</sup> to unidentified species occurs as the catalysis

**Table 1.** 1-octyne hydroboration catalyzed by Zn(II) cations [3a]<sup>+</sup>, [3b]<sup>+</sup>, [5]<sup>+</sup> and [(IPr)ZnC<sub>6</sub>F<sub>5</sub>]<sup>+</sup>.<sup>[a]</sup>

Entry	Cat.	Solvent	T [°C]	t [h]	NMR yield [%] in hydroboration product <b>A</b> <sup>[b]</sup>
1	[3a][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	24	13
2	[3a][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	79	50
3	[3a][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>[c]</sup>	C <sub>6</sub> D <sub>5</sub> Br	50	6	50
4	[3b][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	24	12
5	[3b][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	74	57
6	[3b][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>[c]</sup>	C <sub>6</sub> D <sub>5</sub> Br	50	6	50
7	[5][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	24	77
8	[5][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>[c]</sup>	C <sub>6</sub> D <sub>5</sub> Br	50	3	32
9	[(IPr)ZnC <sub>6</sub> F <sub>5</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	CD <sub>2</sub> Cl <sub>2</sub>	RT	24	27

[a] Conditions: NMR scale reactions, [Cat] = 0.017 M, 20 equiv. 1-octyne, 20 equiv. pinB-H. [b] as determined by <sup>1</sup>H NMR. [c] A black precipitate, presumably Zn<sup>0</sup>, formed within minutes upon heating.

proceeds.<sup>[21]</sup> When performed at 50 °C, though higher hydroboration activities were reached (entries 3, 6 and 8, Table 1), all Zn cations decompose within minutes with the formation of a black insoluble precipitate, presumably Zn<sup>0</sup>, and unidentified species in solution (from <sup>1</sup>H NMR data). Cations [3a]<sup>+</sup>, [3b]<sup>+</sup> and [5]<sup>+</sup> also catalyze the hydroboration of internal alkynes such as 2-hexyne (Table 2), but the catalysis is slower that with 1-octyne and less selective. Thus, hydroboration of 2-hexyne with pinBH catalyzed by [3a]<sup>+</sup>, [3b]<sup>+</sup> and [5]<sup>+</sup> slowly proceeds at room temperature to afford a mixture of vinylboranes **B** (major product) and **C**, both arising from a *cis*-hydroboration addition. At best, starting from 20 equiv. of 2-hexyne and pinBH, 78% conversion of both reagents to an 78/22 **B/C** mixture was achieved after 96 h (CD<sub>2</sub>Cl<sub>2</sub>, RT), as deduced from NMR and GC-MS data (entry 4, Table 2). Upon heating at 50 °C, decomposition of the Zn<sup>II</sup> cations as well as consumption of pinB–H and 2-hexyne to unidentified species occurred though no hydroboration products were detected.

As stated above, the more Lewis acidic Zn–C<sub>6</sub>F<sub>5</sub> cation [5]<sup>+</sup> and [(IPr)ZnC<sub>6</sub>F<sub>5</sub>]<sup>+</sup> retain their integrity throughout alkyne hydroboration catalysis, in line with a Lewis-acid-type catalysis. To get more insight on substrates activation by these Zn<sup>II</sup> organocations, the stability of pinBH/alkyne adducts of model cation **5'** were DFT-estimated (ωB97XD/6-31+G\*\*) leading to models **5'-pinBH** and **5'-Alkyne** (Scheme 2). Model **5'-pinBH** shows that coordination of pinBH to the Zn center of **5'** through a B–O oxygen bond is thermodynamically slightly favored (ΔH = –14.3 kcal/mol and ΔG = –0.2 kcal/mol), and such adduct is thus a viable intermediate under the studied catalytic

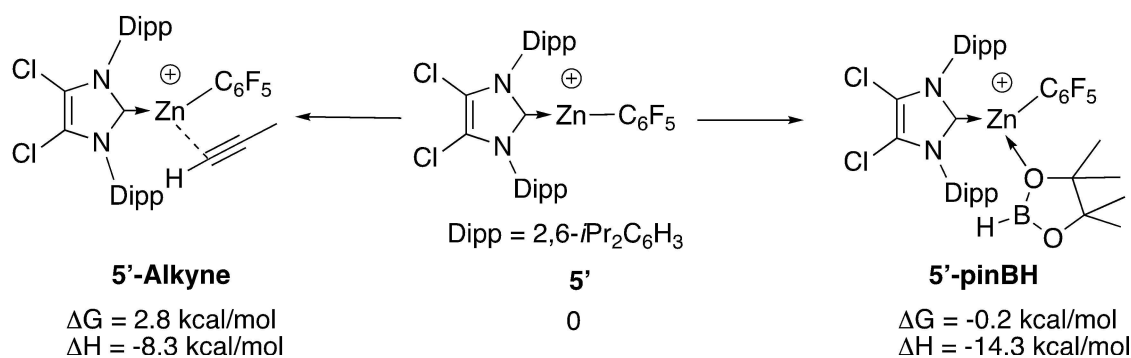
conditions. The formation of the alkyne adduct **5'-Alkyne** is less favored (ΔH = –8.3 kcal/mol and ΔG = 2.5 kcal/mol). From the pinacol borane adduct **5'-pinBH** and as depicted in Scheme 3, it seems possible that alkyne hydroboration proceeds through a B–H insertion reaction between borane adduct **5'-pinBH**, a reaction promoted and driven by a more electrophilic and borenium-like B<sup>III</sup> center due to Zn<sup>II</sup> activation/coordination. Subsequent de-coordination would then afford the *cis*-hydroboration product and re-generate **5'**. Borenium B–H cations are known to readily undergo B–H insertion reactivity with various alkynes to afford the corresponding *cis*-hydroboration vinylborane products.<sup>[22]</sup> In addition, Lewis acid activation (by similar Zn<sup>II</sup> organocations) of pinBH for borenium-type reactivity was recently proposed to be an operative mechanism for Zn-catalyzed C–H borylation of heteroarenes.<sup>[12a]</sup>

In summary, robust and stable two-coordinate Zn<sup>II</sup> cations of the type [(NHC)Zn–R]<sup>+</sup> (R = alkyl, C<sub>6</sub>F<sub>5</sub>) may be accessible using NHCs such as t<sup>l</sup>Bu and IPrCl, showing such Zn<sup>II</sup> organocations may be sterically and electronically tuned by the NHC ligand. Based on FIA estimations, cation [(IPrCl)Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> is the most Lewis acidic among [(NHC)Zn–R]<sup>+</sup> cations thus far studied. The scope of reactivity of these cations was also extended to their use in alkyne hydroboration catalysis. The reaction may proceed at room temperature and likely occurs through a Lewis-acid type mechanism in the case of [Zn–C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> derivatives.

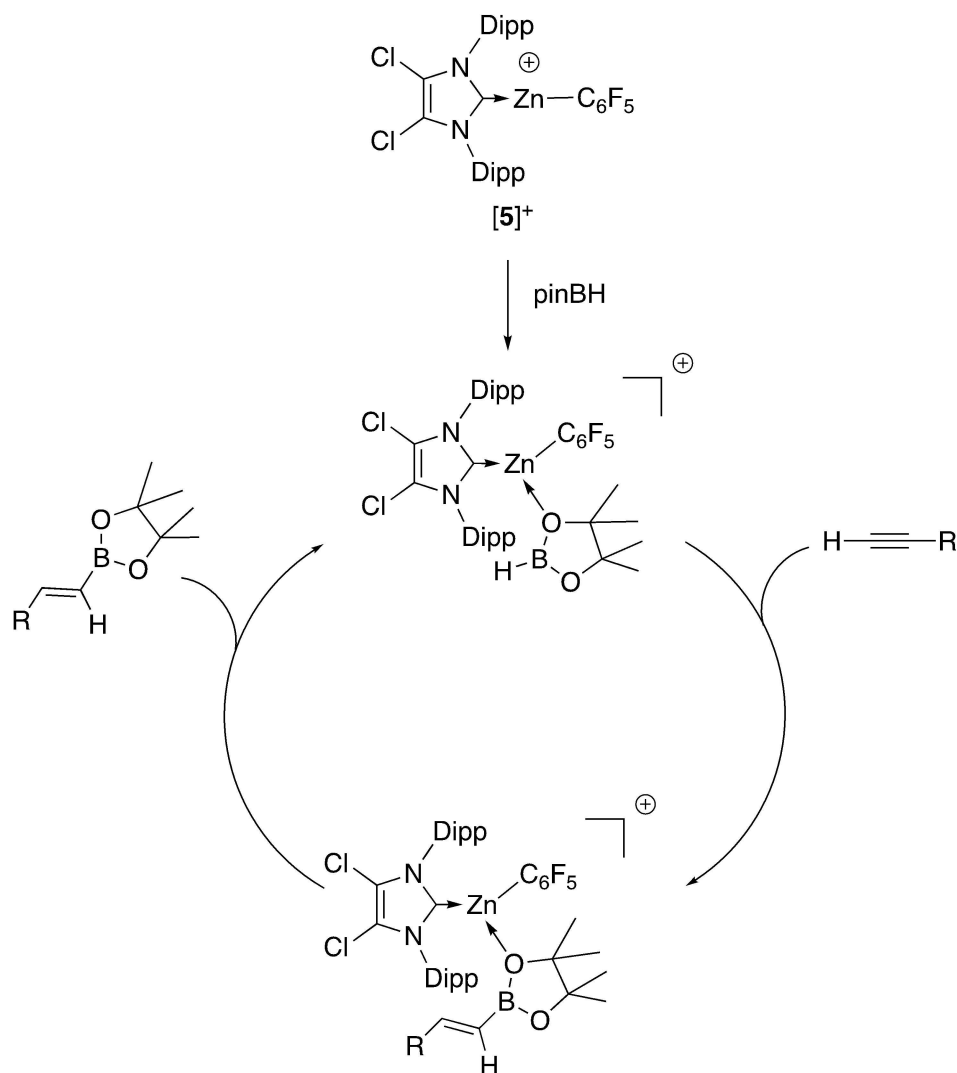
**Table 2.** 1-octyne hydroboration catalyzed by Zn<sup>II</sup> cations [3a]<sup>+</sup>, [3b]<sup>+</sup> and [5]<sup>+</sup>.<sup>[a]</sup>

Entry	Cat.	t [h]	NMR yield (%) in hydroboration products <b>B</b> + <b>C</b> <sup>[b]</sup>	<b>B/C</b> ratio <sup>[b]</sup>
1	[3a][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	96	48	69/31
2	[3b][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	96	39	63/37
3	[5][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	67	69	80/20
4	[5][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	96	78	78/22

[a] Conditions: NMR scale reactions run at RT in CD<sub>2</sub>Cl<sub>2</sub>, [Cat] = 0.017 M, 20 equiv. 2-hexyne, 20 equiv. pinB–H. [b] as determined by <sup>1</sup>H NMR.



**Scheme 2.** Modelled Zn<sup>II</sup> cations **5'**, **5'-pinBH** and **5'-Alkyne** and their relative thermodynamic stability.



Scheme 3. Possible mechanism for terminal alkyne hydroboration catalyzed by cation  $[5]^+$ .

## Experimental Section

**Material, reagents and experimental methods.** All work was performed under  $N_2$  atmosphere using standard glove box techniques. Solvents were stored over 4 Å molecular sieves and were freshly distilled under argon from sodium-benzophenone or  $CaH_2$ , or they were dispensed from a commercial solvent purification system. Deuterated solvents were used as received and stored over 4 Å molecular sieves. NMR spectra were recorded on Bruker Avance I – 300 MHz, Bruker Avance III – 400 MHz, Bruker Avance II – 500 MHz and Bruker Avance III – 600 MHz spectrometers. NMR chemical shift values were determined relative to the residual protons in  $C_6D_6$ ,  $C_6D_5Br$ ,  $CD_2Cl_2$  and  $CDCl_3$  as internal reference for  $^1H$  ( $\delta$  of the most downfield signal = 7.16, 7.30, 5.32, 7.26 ppm) and  $^{13}C\{^1H\}$  ( $\delta$  of the most downfield signal = 128.39, 130.89, 53.84, 77.23 ppm). Pinacolborane,  $Et_3PO$ , 1-octyne, and 2-hexyne were purchased from Aldrich. 1-octyne and 2-hexyne were stored over activated molecular sieves (4 Å) for a least 24 h prior to use.  $ZnMe_2$ ,  $ZnEt_2$ , and  $[CPh_3][B(C_6F_5)_4]$  were obtained from Strem Chemicals Inc as used as received.  $B(C_6F_5)_3$  was obtained from Strem and recrystallized from cold pentane prior to use. The N-heterocyclic carbene 1,3-bis[2,6-bis(1-methylethyl)phenyl]-4,5-dichloro-2H-imidazol-2-ylidene (IPrCl) was prepared according to a literature

procedure.<sup>[23]</sup> GC-MS analysis was conducted on a GC System 7820 A (G4320) connected to a MSD block 5977E (G7036 A) using Agilent High Resolution Gas Chromatography Column HP-5MS UI, 30 m  $\times$  0.250 mm  $\times$  0.25  $\mu$ m.

**Typical procedure for the synthesis of neutral precursors  $[(IPrCl)ZnR_2]$  (1a, R=Et; 1b, R=Me) and  $[(ItBu)ZnEt_2]$  (2).** In a glovebox,  $ZnR_2$  (1 equiv) was added at room temperature *via* a microsyringe to a stirring toluene solution (1 mL) of the corresponding free carbene (1 equiv). The solution was stirred at room temperature for 30 min. It was then cooled at  $-35^\circ C$  overnight leading to the precipitation of a solid. The latter was filtered and then dried under vacuum to afford an analytically pure solid.<sup>[24]</sup>

**$[(IPrCl)ZnEt_2]$  (1a).** Reactants:  $ZnEt_2$  (22.5  $\mu$ L, 0.219 mmol) and IPrCl (100.0 mg, 0.219 mmol). Pale yellow powder (110 mg, 87% yield). Anal. Calcd for  $C_{31}H_{44}Cl_2N_2Zn$  (580.98): C 64.09; H 7.63; N 4.85; Found: C 64.09; H 7.63; N 4.82.  $^1H$  NMR (300 MHz,  $C_6D_6$ ):  $\delta$  = -0.20 (q, 4H,  $ZnCH_2CH_3$ ), 0.77 (t, 6H,  $ZnCH_2CH_3$ ), 1.11 (d, 12H,  $CH_3-iPr$ ), 1.29 (d, 12H,  $CH_3-iPr$ ), 2.67 (m, 4H,  $CH-iPr$ ), 7.11 (d, 4H, CH phenyl), 7.25 (t, 2H, CH phenyl).  $^{13}C\{^1H\}$  NMR (75 MHz,  $C_6D_6$ ):  $\delta$  = 5.1 ( $ZnCH_2CH_3$ ), 14.2 ( $ZnCH_2CH_3$ ), 23.8 ( $CH_3-iPr$ ), 24.1 ( $CH_3-iPr$ ), 29.2



(CH-*i*Pr), 119.2 (C-Cl), 124.6 (m-CH), 131.2 (p-CH), 132.5 (*ipso*-C), 146.0, 192.6 (C<sub>carbene</sub>).

**[(IPrCl)ZnMe<sub>2</sub>] (1b).** Reactants: ZnMe<sub>2</sub> (15.0 μL, 0.219 mmol) and IPrCl (100.0 mg, 0.219 mmol). Colorless powder (111 mg, 92% yield). Anal. Calcd for C<sub>29</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>2</sub>Zn (552.93): C 62.99; H 7.29; N 5.07; Found: C 62.81; H 7.28; N 5.07. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ = -0.90 (s, 6H, ZnCH<sub>3</sub>), 1.11 (d, 12H, CH<sub>3</sub>-*i*Pr), 1.28 (d, 12H, CH<sub>3</sub>-*i*Pr), 2.68 (m, 4H, CH-*i*Pr), 7.11 (d, 4H, CH phenyl), 7.25 (t, 2H, CH phenyl). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ = -7.9 (ZnCH<sub>3</sub>), 23.8 (CH<sub>3</sub>-*i*Pr), 24.1 (CH<sub>3</sub>-*i*Pr), 29.3 (CH-*i*Pr), 119.3 (C-Cl), 124.6 (m-CH), 131.3 (p-CH), 132.5 (*ipso*-C), 146.0, 192.4 (C<sub>carbene</sub>).

**[(*t*Bu)ZnEt<sub>2</sub>] (2).** Reactants: ZnEt<sub>2</sub> (57.0 μL, 0.555 mmol) and *t*Bu (100.0 mg, 0.555 mmol). Colorless powder (146 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.72 (q, 4H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.28 (s, 18H, *t*Bu), 1.78 (t, 6H, ZnCH<sub>2</sub>CH<sub>3</sub>), 6.42 (s, 2H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 4.5 (ZnCH<sub>2</sub>CH<sub>3</sub>), 15.4 (ZnCH<sub>2</sub>CH<sub>3</sub>), 30.5 (CH<sub>3</sub>-*t*Bu), 57.4 (C-*t*Bu), 117.3 (CH), 186.0 (C<sub>carbene</sub>).

**Typical procedure for the synthesis of salt species [(IPrCl)ZnR][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([3a]<sup>+</sup>, R=Et; [3b]<sup>+</sup>, R=Me) and [(*t*Bu)ZnEt][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** In a glovebox, a PhF (0.5 mL) solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was added dropwise (via a pipette) at room temperature to a PhF (0.5 mL) solution of the corresponding neutral NHC-Zn adduct **1a**, **1b** or **2** (1 equiv), leading to the precipitation (within minutes) of a colorless solid. Upon completion of the addition, the reaction mixture was stirred at room temperature for 30 min, filtered and the collected solid was washed three times (3 × 3 mL) with pentane. Except for salt [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (isolated in a pure form after drying *in vacuo*), all solid products were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane and then dried under vacuum to afford the corresponding salts [3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as off-white powders.

**[(IPrCl)ZnEt][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** Reactants: compound **2a** (100.0 mg, 0.172 mmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (159.0 mg, 0.172 mmol). Off-white powder (201 mg, 95% yield). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -0.40 (q, 4H, ZnCH<sub>2</sub>CH<sub>3</sub>), 0.62 (t, 6H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.22 (d, 12H, CH<sub>3</sub>-*i*Pr), 1.33 (d, 12H, CH<sub>3</sub>-*i*Pr), 2.37 (m, 4H, CH-*i*Pr), 7.51 (d, 4H, CH phenyl), 7.73 (t, 2H, CH phenyl). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 6.6 (ZnCH<sub>2</sub>CH<sub>3</sub>), 9.3 (ZnCH<sub>2</sub>CH<sub>3</sub>), 23.5 (CH<sub>3</sub>-*i*Pr), 25.5 (CH<sub>3</sub>-*i*Pr), 29.7 (CH-*i*Pr), 123.6 (C-Cl), 126.3 (m-CH), 128.8, 134.0 (p-CH), 136.6 (dm, *J*<sub>CF</sub> = 239 Hz, m-C<sub>6</sub>F<sub>5</sub>), 138.6 (dm, *J*<sub>CF</sub> = 235 Hz, p-C<sub>6</sub>F<sub>5</sub>), 146.3 (C-Ar), 148.5 (dm, *J*<sub>CF</sub> = 241 Hz, o-C<sub>6</sub>F<sub>5</sub>), 164.4 (C<sub>carbene</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -134.1 (br, o-F), -164.7 (t, *J*<sub>FF</sub> = 20.4 Hz, p-F), -168.6 (bt, m-F).

**[(IPrCl)ZnMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** Reactants: compound **2b** (100.0 mg, 0.181 mmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (167.0 mg, 0.181 mmol). Off-white powder (209 mg, 95% yield). Anal. Calcd for C<sub>52</sub>H<sub>37</sub>BCl<sub>2</sub>F<sub>20</sub>N<sub>2</sub>Zn (1216.93): C 51.32; H 3.06; N 2.30; Found: C 51.43; H 3.45; N 2.16. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -0.54 (s, 6H, ZnCH<sub>3</sub>), 1.23 (d, 12H, CH<sub>3</sub>-*i*Pr), 1.33 (d, 12H, CH<sub>3</sub>-*i*Pr), 2.37 (m, 4H, CH-*i*Pr), 7.49 (d, 4H, CH phenyl), 7.73 (t, 2H, CH phenyl). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -9.0 (ZnCH<sub>3</sub>), 23.7 (CH<sub>3</sub>-*i*Pr), 25.4 (CH<sub>3</sub>-*i*Pr), 29.8 (CH-*i*Pr), 123.7 (C-Cl), 126.3 (m-CH), 128.8, 134.0 (p-CH), 136.6 (dm, *J*<sub>CF</sub> = 239 Hz, m-C<sub>6</sub>F<sub>5</sub>), 138.6 (dm, *J*<sub>CF</sub> = 235 Hz, p-C<sub>6</sub>F<sub>5</sub>), 146.3 (C-Ar), 148.5 (dm, *J*<sub>CF</sub> = 241 Hz, o-C<sub>6</sub>F<sub>5</sub>), 164.2 (C<sub>carbene</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -134.1 (br, o-F), -164.7 (t, *J*<sub>FF</sub> = 20.4 Hz, p-F), -168.6 (bt, m-F).

**[(*t*Bu)ZnEt][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** Reactants: compound **2** (100 mg, 0.329 mmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (304 mg, 0.329 mmol). Off-white powder (276 mg, 88% yield). Anal. Calcd for C<sub>37</sub>H<sub>25</sub>BF<sub>20</sub>N<sub>2</sub>Zn (953.77): C 46.59; H 2.64; N 2.94; Found: C 46.87; H 2.68; N 2.88. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ = 0.64 (q, 4H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.13 (t, 6H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.23 (s, 18H, *t*Bu), 6.86 (s, H-C4/C5 carbene). <sup>19</sup>F NMR (282 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ = -131.4 (br, o-F anion), -161.6 (t, *J*<sub>FF</sub> = 20.4 Hz, p-F anion), -165.5 (bt, m-F anion).

**Typical procedure for the synthesis of salt species [(IPrCl)ZnC<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) and [(*t*Bu)ZnC<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([6][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** In a glovebox, a PhF (0.5 mL) solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was added dropwise (via a pipette) at room temperature to a PhF (0.5 mL) solution of the corresponding Zn-R<sup>+</sup> cation [3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1 equiv), leading to the precipitation (within minutes) of a colorless solid. Upon completion of the addition, the reaction mixture was stirred at room temperature for 24 h and the volatiles were evaporated *in vacuo*. The resulting oily residue was triturated with pentane (5 mL) leading to the formation of a colorless solid. The latter was collected, washed three times with pentane (3 × 3 mL) and then dried under vacuum to afford the corresponding salt [5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [6][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as analytically pure off-white powders.

**[(IPrCl)ZnC<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** Reactants: compound [3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (100.0 mg, 0.081 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (42.0 mg, 0.082 mmol). Off-white powder (101 mg, 90% yield). Anal. Calcd for C<sub>57</sub>H<sub>34</sub>BCl<sub>2</sub>F<sub>25</sub>N<sub>2</sub>Zn (1368.95): C 50.01; H 2.50; N 2.05; Found: C 49.72; H 2.70; N 2.04. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.23 (d, 12H, CH<sub>3</sub>-*i*Pr), 1.32 (d, 12H, CH<sub>3</sub>-*i*Pr), 2.40 (m, 4H, CH-*i*Pr), 7.46 (d, 4H, CH phenyl), 7.71 (t, 2H, CH phenyl). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 24.0 (CH<sub>3</sub>-*i*Pr), 24.8 (CH<sub>3</sub>-*i*Pr), 29.9 (CH-*i*Pr), 124.5 (C-Cl), 126.4 (m-CH), 129.0, 134.1 (p-CH), 136.6 (dm, *J*<sub>CF</sub> = 239 Hz, m-C<sub>6</sub>F<sub>5</sub>), 138.6 (dm, *J*<sub>CF</sub> = 235 Hz, p-C<sub>6</sub>F<sub>5</sub>), 146.3 (C-Ar), 148.5 (dm, *J*<sub>CF</sub> = 241 Hz, o-C<sub>6</sub>F<sub>5</sub>), 161.6 (C<sub>carbene</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -116.5 (m, o-ZnC<sub>6</sub>F<sub>5</sub>), -134.1 (br, o-F anion), -149.1 (t, *J*<sub>FF</sub> = 19.2 Hz, p-ZnC<sub>6</sub>F<sub>5</sub>), -158.8 (m, m-ZnC<sub>6</sub>F<sub>5</sub>), -163.8 (t, *J*<sub>FF</sub> = 20.4 Hz, p-F anion), -167.6 (bt, m-F anion).

**[(*t*Bu)ZnC<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([6][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).** Reactants: compound [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (100.0 mg, 0.104 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (53.7 mg, 0.104 mmol). Off-white powder (96 mg, 85% yield). Anal. Calcd for C<sub>41</sub>H<sub>20</sub>BF<sub>25</sub>N<sub>2</sub>Zn (1091.76): C 45.10; H 1.85; N 2.57; Found: C 45.47; H 2.15; N 2.54. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ = 1.36 (s, 18H, *t*Bu), 6.98 (s, H-C4/C5 carbene). <sup>19</sup>F NMR (282 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ = -116.1 (m, o-ZnC<sub>6</sub>F<sub>5</sub>), -131.4 (br, o-F anion), -148.5 (t, *J*<sub>FF</sub> = 19.2 Hz, p-ZnC<sub>6</sub>F<sub>5</sub>), -157.6 (m, m-ZnC<sub>6</sub>F<sub>5</sub>), -161.6 (t, *J*<sub>FF</sub> = 20.4 Hz, p-F anion), -165.5 (bt, m-F anion).

**Typical procedure for alkyne hydroboration catalysis mediated NHC-supported Zn cations.** A J-Young valve NMR tube was charged with a solution of the appropriate Zn catalyst (8.7 μmol) in CD<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>D<sub>5</sub>Br (0.5 mL), 1-octyne or 2-hexyne (174 μmol, 20 equiv. vs. catalyst) and pinacolborane (174 μmol, 20 equiv. vs. catalyst). A <sup>1</sup>H NMR spectrum was immediately recorded after mixing all reagents and the residual silicone grease peak (δ = 0.09 and 0.11 ppm in CD<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>D<sub>5</sub>Br, respectively) was systematically used as an internal standard for all catalytic runs. The NMR tube was placed at the desired temperature and the reaction was monitored by <sup>1</sup>H NMR spectroscopy, showing the formation of hydroboration products **A** or **B/C**, by comparison with literature NMR data.<sup>[26]</sup> After completion of the reaction, the volatiles were removed under vacuum for 1 h and the residue extracted with wet pentane. The identity of the hydroboration products and the selectivity of the catalysis were further confirmed by GC-MS analysis. GC/MS: **A**; t<sub>R</sub> = 5.28 min, m/z 238.1 (M<sup>+</sup>), 223.1 (M<sup>+</sup> - 15(Me)). **B**; t<sub>R</sub> = 4.19 min, m/z 210.2 (M<sup>+</sup>), 195.1 (M<sup>+</sup> - 15(Me)). **C**; t<sub>R</sub> = 4.02 min, m/z 210.2 (M<sup>+</sup>), 195.1 (M<sup>+</sup> - 15(Me)).

**Crystallographic data for complexes [(IPrCl)ZnMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), [(IPrCl)ZnMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) [(IPrCl)ZnC<sub>6</sub>F<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>])**

Single crystals of complexes [3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were grown from slow diffusion of pentane in a CH<sub>2</sub>Cl<sub>2</sub> solution. X-Ray diffraction data collection was carried out on a

Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)<sup>[27]</sup> from reflections taken from tree sets of 12 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-97.<sup>[28]</sup> The refinement and all further calculations were carried out using SHELXL-97.<sup>[29]</sup> The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. A summary of crystal data and structure refinement details for [3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] are provided in Tables S1–S3 (Supporting Information).

Deposition Numbers 2113797 (for [3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), 2113798 (for [4][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), and 2113799 (for [5][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

- [1] S. P. Nolan, *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, 2006.
- [2] S. Díez-González, *N-Heterocyclic Carbenes, From Laboratories Curiosities to Efficient Synthetic Tools*, RSC Catalysis Series, RSC Publishing, Cambridge, 2011.
- [3] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed.* **1997**, *36*, 2162–2187; *Angew. Chem.* **1997**, *109*, 2256–2282.
- [4] R. H. Crabtree, *Coord. Chem. Rev.* **2013**, *257*, 755–766.
- [5] A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921.
- [6] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92.
- [7] V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678–9842.
- [8] A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994–7112.
- [9] S. Khan, H. W. Roesky, *Chem. Eur. J.* **2019**, *25*, 1636–1648.
- [10] Y. Wang, G. H. Robinson, *Dalton Trans.* **2012**, *41*, 337–345.

- [11] a) D. Specklin, C. Fliedel, S. Dagorne, *Chem. Rec.* **2021**, *21*, 1130–1143; b) S. Dagorne, *Synthesis* **2018**, *50*, 3662–3670; c) S. Budagumpi, S. Endud, *Organometallics* **2013**, *32*, 1537–1562.
- [12] Selected recent examples: a) M. E. Grundy, K. Yuan, G. S. Nichol, M. J. Ingleson, *Chem. Sci.* **2021**, *12*, 8190–8198; b) J.-C. Bruyere, D. Specklin, C. Gourlaouen, R. Lapenta, L. F. Veiros, A. Grassi, S. Milione, L. Ruhlmann, C. Boudon, S. Dagorne, *Chem. Eur. J.* **2019**, *25*, 8061–8069; c) R. J. Procter, M. Uzelac, J. Cid, P. J. Rushworth, M. J. Ingleson, *ACS Catal.* **2019**, *9*, 5760–5771; d) D. Specklin, F. Hild, C. Fliedel, C. Gourlaouen, L. F. Veiros, S. Dagorne, *Chem. Eur. J.* **2017**, *23*, 15908–15912; e) A. Rit, A. Zanardi, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2014**, *53*, 13273–13277; *Angew. Chem.* **2014**, *126*, 13489–13493; f) C. Fliedel, D. Vila-Vicosa, M. J. Calhorda, S. Dagorne, T. Avilés, *ChemCatChem* **2014**, *6*, 1357–1367.
- [13] M. Bochmann, *Coord. Chem. Rev.* **2009**, *253*, 2000–2014.
- [14] J. Tian, Y. Chen, M. Vayer, A. Djurovic, R. Guillot, R. Guermazi, S. Dagorne, C. Bour, V. Gandon, *Chem. Eur. J.* **2020**, *26*, 12831–12838.
- [15] D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723–6753.
- [16] a) G. Schnee, C. Fliedel, T. Avilés, S. Dagorne, *Eur. J. Inorg. Chem.* **2013**, 3699–3709; b) A. Rit, T. P. Spaniol, L. Maron, J. Okuda, *Organometallics* **2014**, *33*, 2039–2047.
- [17] A. J. Arduengo, H. V. R. Dias, F. Davidson, R. L. Harlow, *J. Organomet. Chem.* **1993**, *462*, 13–18.
- [18] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806–5812.
- [19] Representative examples of structurally characterized compounds with Zn–F bonds: a) W. Sattler, S. Ruccolo, G. Parkin, J. Am, *Chem. Soc. Rev.* **2013**, *135*, 18714–18717; b) M. Tesmer, M. Shu, H. Vahrenkamp, *Inorg. Chem.* **2001**, *40*, 4022; c) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, E. Macedi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi, *Chem. Eur. J.* **2011**, *17*, 1670.
- [20] The FIAs were initially DFT-estimated in the gas phase and led to higher values for [(NHC)Zn–R]<sup>+</sup> cations vs. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; see Ref. 12d. For a discussion on discrepancies between gas and solvent phase FIA values of Lewis acids, see: L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896.
- [21] The possible formation of a Zn hydride cation of the type [(NHC)Zn–H]<sup>+</sup>, through a B–H/Zn–C  $\alpha$ -bond metathesis between pinBH and [3a/3b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], was considered (see Ref. 12c). Though it cannot be excluded, neither such Zn–H cation nor the expected side-product pinB–R (R=Et, Me) were detected by <sup>1</sup>H NMR as the catalysis proceeds. In addition, no pinB–R product was detected by GC-MS analysis of the hydrolyzed final product mixture.
- [22] J. Lam, L. L. Cao, J. M. Farrell, D. W. Stephan, *Dalton Trans.* **2020**, *49*, 1839–1846.
- [23] A. J. Arduengo, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523–14534.
- [24] No satisfactory elemental analysis data could be obtained for **2and** [3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], presumably due its high air- and moisture-sensitivity.
- [25] The low solubility of salt [6][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>D<sub>6</sub>Br and CD<sub>2</sub>Cl<sub>2</sub> precluded the obtainment of <sup>13</sup>C NMR data for [6][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].
- [26] a) A. G. Grirrane, A. Corma, H. Garcia, *Chem. Eur. J.* **2011**, *17*, 2467; b) H. R. Kim, J. Yun, *Chem. Commun.* **2011**, *47*, 2943; c) A. Bismuto, S. P. Thomas, M. J. Cowley, *Angew. Chem. Int. Ed.* **2016**, *55*, 15356.
- [27] *M86-E01078 APEX2 User Manual*, Bruker AXS Inc., Madison, USA, 2006.
- [28] G. M. Sheldrick, *SHELXS-97 Program for Crystal Structure Determination*, *Acta Crystallogr.* **1990**, *A46*, 467.
- [29] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Göttingen, Germany, 1999.

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