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# NHC-stabilized Al(III) and Ga(III) cationic alkyls: Synthesis, structure and use in hydrosilylation catalysis

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# ABSTRACT

Cationic Al(III) and Ga(III) species supported by *N*-heterocyclic carbene (NHC) ligands, (IDipp)  $AIMe_2(PhBr)]^+$  ([1]<sup>+</sup>, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and (IDipp)GaMe\_2]<sup>+</sup> ([2]<sup>+</sup>), were prepared and structurally characterized as  $B(C_6F_5)_4$  salts *via* ionization of the corresponding neutral precursors (IDipp)MMe\_3 (M = AI, Ga) with [Ph\_3C][B(C\_6F\_5)\_4] in PhBr at room temperature. Both [1]  $[B(C_6F_5)_4]$  and [2][ $B(C_6F_5)_4$ ] salt were isolated in high yield and their solid state structures established through X-ray crystallographic studies. Cations [1]<sup>+</sup> and [2]<sup>+</sup>, which are rare examples of structurally characterized tris-organyl Al(III) and Ga(III) cations, stand as potent Lewis acids as experimentally estimated through the Gutmann-Beckett method. These cations were further exploited in hydrosilylation catalysis of alkynes, benzaldehyde and CO<sub>2</sub> using HSiEt<sub>3</sub> as an hydrosilane source. Hydrosilylation of 1-hexyne, 4-phenylbutyne and phenylacetylene led to the formation of the corresponding Z-selective products **3–5**, respectively, while benzaldehyde was converted to PhCH<sub>2</sub>OSiEt<sub>3</sub> (**6**). Cations [1]<sup>+</sup> and [2]<sup>+</sup> also

# 1. Introduction

Ligand-supported well-defined Al(III) species have been widely studied for their structural interest and as Lewis acidic catalysts for various organic transformations [1]. In this regard, cationic Al(III) species are potent electrophilic and Lewis acidic entities with an enhanced Lewis acidity [2], and are known to activate various unsaturated/polar substrates [3,4]. For example, we previously showed that three-/four-coordinate Al alkyl cations bearing N-/Obased chelating ligands mediate hydride transfer reactions to olefins or ketones and effectively polymerize cyclic ethers/esters [5]. Five-/four-coordinate Al(III) cations were also recently exploited as catalysts for the cyanosilylation of carbonyl substrates and the Tishchenko reaction [6]. Strong Lewis acids of the type AlR<sup>+</sup><sub>2</sub> and AlBr<sup>+</sup><sub>2</sub> also catalyze CO<sub>2</sub> hydrosilylation and carbonyl-olefin metathesis, respectively, further illustrating the potential of lowcoordinate Al cations in catalysis [7,8]. Three-coordinate Al cations of the type  $(NacNac)Al-R^+$  (R = H, alkyl) were recently shown to be highly efficient catalysts in alkene hydrosilylation [9]. Yet, the high reactivity of low-coordinate (two-/three-coordinate) Al(III) organometallics comes along with their limited stability in polar media

and a poor functional group tolerance, hindering to some extent their wider use in catalysis.

Due to their exceptional strong  $\sigma$ -donation and steric tunability, N-heterocyclic carbenes (NHCs) are now ubiquitous ligands in organometallic and coordination chemistry since they are able to stabilize various metal/heteroelement complexes [10], including oxophilic and electropositive centers such as group 13 metal M(III) salts (M = Al, Ga, In) [11]. Early examples of Al-NHC species of the type (NHC)AlX<sub>3</sub> were reported in the early 1990's by Arduengo [12], and were found to be more robust and thermally stable than their phosphine adduct analogues. In contrast, NHC-bearing Al(III) cations remain little explored. Several mono- and dicationic Al hydrido species of the type [(NHC)<sub>2</sub>AlH<sub>2</sub>]<sup>+</sup>, [(NHC)AlHI]<sup>+</sup>, [(NHC)<sub>2</sub>- $AI-H]^{2+}$  and  $[(NHC)AIH_2]_2^{2+}$  were recently characterized [13,14]. We also showed that four-coordinate cations of the type (NHC)  $MR_2(L)^+$  (M = Al, Ga, In; L = Et<sub>2</sub>O, THF) were stable and robust cations able to initiate the polymerization of cyclic esters [15]. A few NHC-supported Ga(III) and In(III) halido cations have also been structurally characterized [16]. For enhanced electrophilicity/reactivity, we have become interested into three-coordinate Al(III) and Ga(III) alkyl species of the type (NHC)MR<sub>2</sub><sup>+</sup> (M = Al, Ga) for their structural interest and for subsequent use in activation/functionalization catalysis. As part of these studies, we here report on the synthesis and structural characterization of Al(III) and Ga(III) cationic alkyls of the types (NHC)AlMe<sup>+</sup><sub>2</sub> and (NHC)GaMe<sup>+</sup><sub>2</sub>. Such strong





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electrophiles were exploited in aldehyde, alkyne and CO<sub>2</sub> hydrosilylation catalysis, as also discussed herein.

# 2. Results – Discussion

# 2.1. Synthesis and structure of the Al-NHC and Ga-NHC cations (IDipp) $MMe_2^+$ (M = Al, Ga). [1][ $B(C_6F_5)_4$ ] and [2][ $B(C_6F_5)_4$ ]

Cations 1<sup>+</sup> and 2<sup>+</sup> were prepared *via* a methide abstraction reaction of the corresponding neutral precursors (IDipp)AlMe3 and (IDipp)GaMe<sub>3</sub> (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [15], a methodology well-established in the literature [2,3]. Thus, the ionization reaction of  $(IDipp)MMe_3$  (M = Al, Ga) and 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  (PhBr, room temperature) led to the quantitative formation of cations  $[(IDipp)AIMe_2]^+$  (1<sup>+</sup>) and  $[(IDipp)GaMe_2]^+$  (2<sup>+</sup>), respectively, as B  $(C_6F_5)_4^-$  salts (Scheme 1), as deduced from NMR data. Both cations,  $[1][B(C_6F_5)_4]$  and  $[2][B(C_6F_5)_4]$ , were isolated in high yield as analytically pure colorless solids. In solution, both salts are unstable in CH<sub>2</sub>Cl<sub>2</sub> and decomposes within minutes at room temperature to unknown species, likely reflecting the strong Lewis acidity of cations  $1^+$  and  $2^+$  [17]. In contrast, the earlier reported [(NHC)MR<sub>2</sub>(L)]<sup>+</sup>  $(M = AI, Ga; L = Et_2O, THF)$  cations are stable for days in  $CH_2Cl_2$  confirming that Lewis bases such as Et<sub>2</sub>O and THF significantly quench the Lewis acidity of the  $(NHC)MR_2^+$  (M = Al, Ga) moiety.

Cations  $\mathbf{1}^+$  and  $\mathbf{2}^+$  are however stable for days in PhBr under inert atmosphere. The <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR data for  $[\mathbf{1}][B(C_6F_5)_4]$ and  $[\mathbf{2}][B(C_6F_5)_4]$  ( $C_6D_5Br$ , room temperature) agree with the proposed formulation for cations  $\mathbf{1}^+$  and  $\mathbf{2}^+$  with no evidence of cation/anion interactions in solution. For instance, in the case of the Al cation  $\mathbf{1}^+$ , characteristic <sup>1</sup>H NMR resonances include: 1) a significantly downfield shifted <sup>1</sup>H NMR chemical shift for the *H*-C4/C5 NHC resonance ( $\delta$  7.02 ppm) *vs.* that in neutral precursor (IDipp)AlMe<sub>3</sub> ( $\delta$  6.58 ppm), in line with NHC coordination with the more electrophilic [AlR<sub>2</sub>]<sup>+</sup> moiety; 2) an upfield shifted *C*<sub>carbene</sub> <sup>13</sup>C NMR signal ( $\delta$  163.0 *vs.* 178.3 ppm in (IDipp)AlMe<sub>3</sub>) reflecting an enhanced Lewis acidity of the Al(III) center in cation  $\mathbf{1}^+$ .

Though no solvent (PhBr) interaction/coordination were observed in solution for  $\mathbf{1}^+$  and  $\mathbf{2}^+$  under the studied conditions, fast coordination/de-coordination of PhBr to the M(III) cation, at least in the case of the more Lewis acidic Al derivative, seems probable and certainly stabilize these electrophiles: the latter is suggested by the solid-state structure of the Al(III) cation  $\mathbf{1}^+$  as an Al–PhBr adduct. Thus, the molecular structure of salt [1][B ( $C_6F_5$ )<sub>4</sub>], crystallized from a PhBr/pentane solution, was confirmed through X-ray crystallographic analysis. Salt [1][B( $C_6F_5$ )<sub>4</sub>]<sup>-</sup> anions

with no cation/anion interactions (Fig. S7, SI). As shown in Fig. 1, the Al cation [1-PhBr]<sup>+</sup> consists of a [AlMe<sub>2</sub>]<sup>+</sup> moiety stabilized by one IDipp carbene and the coordination of PhBr through the Br atom. To our knowledge, [1-PhBr]<sup>+</sup> is first structurally characterized PhBr adduct of an Al(III) species and its formation clearly substantiates the strong Lewis acidity of the Al(III) center in 1<sup>+</sup>. The Al-Br bond distance (2.663(1) Å) lies in the upper range of Al-Br-Al bond distances and is a bit shorter than that found in a vinylic Al(III) species containing a dative Al–Br bond (2.703(8) Å) [18,19]. The latter is consistent with an effective coordination of PhBr to the Al(III) center in [**1-PhBr**]<sup>+</sup>. PhBr coordination causes a slight pyramidalization of the geometry around the Al(III) center in [(IDipp)AlMe<sub>2</sub>]<sup>+</sup>, as reflected by the sum of C-Al-C bond angles (around 351°). The Al- $C_{\text{NHC}}$  bond distance in  $[1-PhBr]^+$  (2.045(4) Å) is similar to that in cation  $[(IMes)Al(OEt_2)Me_2]^+$  (2.066(4) Å) and expectedly shorter than that in neutral precursor (IDipp)AlMe<sub>3</sub> (2.103(3) Å) [20].

The molecular structure of the Ga(III) salt  $[\mathbf{2}][B(C_6F_5)_4]$ , crystallized from PhBr/toluene, was also confirmed through X-ray crystallographic analysis, and consists of discrete  $[\mathbf{2}]^+$  and  $[B(C_6F_5)_4]^-$  ions with no cation/anion interactions (Fig. S8, SI). As depicted in Fig. 2, cation  $[\mathbf{2}]^+$  features a central three-coordinate Ga(III) center in a trigonal geometry. The effective coordination of IDipp to the  $[GaMe_2]^+$  group is shown by a much shorter Ga-C<sub>NHC</sub> bond distance (2.018(3) Å) than in (IDipp)GaMe\_3 precursor (2.105(4) Å) [19]. The absence of PhBr coordination to the Ga(III) center in  $[\mathbf{2}]^+$  presumably indicates the lower Lewis acidity of Ga(III) vs. Al(III).

Cations  $[1]^{*}$  and  $[2]^{*}$  immediately reacted with 1 equiv Et<sub>2</sub>O or THF (C<sub>6</sub>D<sub>5</sub>Br, room to form the corresponding four-coordinate cationic adducts [(NHC)MR<sub>2</sub>(L)]<sup>\*</sup> (M = Al, Ga; L = Et<sub>2</sub>O, THF), as deduced from comparison of NMR data with literature [15]. Since  $[1]^{*}$  and  $[2]^{*}$  stand as potentially strong Lewis acids and their Lewis acidity was thus experimentally estimated using the Gutmann-Beckett method and compiled in Table 1 [21]. According to these measurements, the Lewis acidity of the Al cation  $[1]^{*}$  is similar to that of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, a landmark Lewis acid ( $\Delta\delta^{31}P$  (C<sub>6</sub>D<sub>5</sub>Br) = 76.2 and 76.6 ppm for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and  $[1]^{*}$ , respectively). The Ga cation  $[2]^{*}$  appears to be slightly less Lewis acidic ( $\Delta\delta^{31}P$  (C<sub>6</sub>D<sub>5</sub>Br) = 73.2 ppm), in line with other structural data.



Scheme 1. Synthesis of the NHC-supported Al(III) and Ga(III) species  $[1{\rm --}2][B\ (C_6F_5)_4]$ 



**Fig. 1.** Molecular structure of the Al cation [1]<sup>+</sup> (ORTEP view; ellipsoids enclose 50% electronic density) with selected atom labeling for clarity. The hydrogen atoms are omitted for clarity.



**Fig. 2.** Molecular structure of the Ga cation [**2**]<sup>+</sup> (ORTEP view; ellipsoids enclose 50% electronic density) with selected atom labeling for clarity. The hydrogen atoms are omitted for clarity.

# 2.2. Alkene/alkyne hydrosilylation catalysis mediated by $[1-2][B (C_6F_5)_4]$

The Lewis acidic Al and Ga salts  $[1-2][B(C_6F_5)_4]$  were initially tested in 1-hexene hydrosilylation. As monitored by <sup>1</sup>H NMR, no reaction was observed at room temperature in  $C_6D_5Br$  between  $[1-2][B(C_6F_5)_4]$  (5% mol) and a 1/1 1-hexene/HSiEt<sub>3</sub> mixture (20 equiv *vs.* catalyst). Heating to 65 °C for extended time (days) only led to 1-hexene polymerization, as deduced from NMR and GPC data, along with unreacted HSiEt<sub>3</sub>. The formation of poly(1-hexene) likely occurs *via* a carbocationic Lewis acid-initiated polymerization mechanism, as is well-known for highly electrophilic species [22].

In contrast, as compiled in Table 2, the Al cation  $[1]^+$  was found to be an extremely efficient and selective for alkyne hydrosilylation, allowing the fast and quantitative *trans*-hydrosilylation of 1hexyne, 4-phenylbutyne and phenylacetylene within minutes (5 to 30 min; entries 1, 3 and 5, Table 2) at room temperature using a low catalyst loading (5% mol) to selectively afford the *Z* products **3–5**, respectively (Scheme 2). Catalyst  $[1]^+$  retains its integrity as the catalysis proceeds, which is consistent with  $[1]^+$  solely acting as a Lewis acid. Al-based alkyne hydrosilylation catalysis have thus far been restricted to the use of AlCl<sub>3</sub> as catalyst, yet requiring a much higher catalytic loading (typically 20% mol) and an extremely careful AlCl<sub>3</sub> purification prior to catalysis [23].

The present Al-catalyzed alkyne hydrosilylation likely occur in a similar way to that observed with AlCl<sub>3</sub> with 1,2 *anti*-addition of H–SiEt<sub>3</sub> to the C–C triple bond [22a]. As a comparison, the less Lewis acidic Ga cation  $[2]^+$  is significantly less active in alkyne hydrosilylation (entries 2, 4 and 6, Table 2), and expectedly displays the same selectivity (*trans*-hydrosilylation) with the formation of hydrosilylated products **3–5**.

2.3. Benzaldehyde and  $CO_2$  hydrosilylation catalysis mediated by [1–2]  $[B(C_6F_5)_4]$ 

The potential of Al and Ga cations  $[1]^+$  and  $[2]^+$  as Lewis acidic catalysts for the hydrosilylation of carbonyl substrates was also evaluated. Thus,  $[1]^+$  (5% mol) is highly active in benzaldehyde hydrosilylation at room temperature to lead within 50 min to the quantitative conversion of a 1/1 benzaldehyde/HSiEt<sub>3</sub> mixture to the mono-reduction benzyl silyl ether product **6** (Scheme 3; entry 7, Table 2). Though inactive at room temperature, the less Lewis acidic Ga cation  $[2]^+$  also allowed benzaldehyde reduction to **6** upon heating (entry 8, Table 2). The present benzaldehyde hydrosilylation catalysis likely proceeds through a similar Lewis-acid type activation to that thoroughly studied for borane-mediated Lewis acid catalysis [24].

Despite being a challenging carbonyl substrate for activation/functionalization. CO<sub>2</sub> was recently shown to be reduced to methanol-equivalent MeOSiR<sub>3</sub> products and/or methane by Lewis acidpromoted hydrosilylation, primarily using Al- and Zn-based cations as strong electrophiles [7,25]. Salt  $[1-2][B(C_6F_5)_4]$  were thus probed as CO<sub>2</sub> hydrosilylation catalysts and exhibited moderate performances (entries 9 and 10, Table 2). Thus, in the presence of CO<sub>2</sub> (1.5 atm) and HSiEt<sub>3</sub> (10 equiv vs. catalyst), Al cation  $[1]^+$ slowly but selectively hydrosilylates CO<sub>2</sub> to methanol-equivalent MeOSiEt<sub>3</sub> (C<sub>6</sub>D<sub>5</sub>Br, 90 °C, 41 h , 43% conversion to MeOSiEt<sub>3</sub>), as deduced from NMR and GC-MS data. In line with the observed trend for these systems, the less acidic Ga center  $[2]^+$  showed a similar selectivity but displayed a lower activity (C<sub>6</sub>D<sub>5</sub>Br, 90 °C, 41 h , 15% conversion to MeOSiEt<sub>3</sub>). For both catalysts  $[1]^+$  and [2]<sup>+</sup>, MeOSiEt<sub>3</sub> was the only observed product by <sup>1</sup>H NMR, thus with no NMR detection of the first and second hydrosilylation products, formate HCO<sub>2</sub>SiEt<sub>3</sub> and ketal Et<sub>3</sub>SiO-CH<sub>2</sub>-OSiEt<sub>3</sub>, respectively, as the CO<sub>2</sub> hydrosilylation proceeds. The latter is in line with the initial CO<sub>2</sub> activation/functionalization being rate-limiting, as has been observed for other Lewis acid-type CO<sub>2</sub> hydrosilylation catalysts [7,25], and fast consumption of HCO<sub>2</sub>SiEt<sub>3</sub> to Et<sub>3</sub>SiO-CH<sub>2</sub>-OSiEt<sub>3</sub> and eventually MeOSiEt<sub>3</sub>.

# 3. Conclusion

The present study showed that NHC-supported Al(III) and Ga (III) alkyl cations of the type  $[(NHC)AlMe_2(PhBr)]^+$  and  $[(NHC) GaMe_2]^+$  may be readily prepared as thermally stable yet strongly electrophilic species. Cations [1]<sup>+</sup> and [2]<sup>+</sup>, which are rare structurally characterized tris-organyl Al(III) and Ga(III) cations, are robust Lewis acidic species that may act as effective and selective hydrosilylation catalysts of alkynes, aldehydes and CO<sub>2</sub>. As a comparison, it may be noted that robust four-coordinate [(NHC) MR<sub>2</sub>(L)]<sup>+</sup> (M = Al, Ga; L = Et<sub>2</sub>O, THF) cations displayed no catalytic activity in any of the hydrosilylation reactions studied herein. In line with its stronger Lewis acidity, the Al cation [1]<sup>+</sup> is significantly more active than its Ga analogue [2]<sup>+</sup>, while both cations display identical selectivities across all hydrosilylations. All hydrosilylation catalysis data agree with Lewis acid-mediated processes mediated by [1]<sup>+</sup> and [2]<sup>+</sup>.

Table 1

Lewis acidity assessment of salt  $[1][B(C_6F_5)_4]$  and  $[2][B(C_6F_5)_4]$  via the Gutmann-Beckett method.<sup>a</sup>

	POEt <sub>3</sub>	$B(C_6F_5)_3 + 1 \text{ equiv POEt}_3$	$[1][B(C_6F_5)_4] + 1 \text{ equiv POEt}_3$	$[2][B(C_6F_5)_4] + 1 equiv POEt_3$
<sup>31</sup> P NMR ( $C_6D_5Br$ ) $\delta(ppm)$	46.8	76.2	76.6	73.2

<sup>a</sup> The <sup>31</sup>P NMR chemical shift difference between the Et<sub>3</sub>P = O Lewis adduct and free Et<sub>3</sub>P = O allows an estimation of Lewis acidity [21]. The <sup>31</sup>P NMR measurements were done in C<sub>6</sub>D<sub>5</sub>Br at RT.

Table 2		
Alkyne, benzaldehyde and CO <sub>2</sub> hydrosilylation catalysis results using	$[1-2][B(C_6F_5)_4]$ as catalysts and HSiEt <sub>3</sub> as an hydrosila	ne source. <sup>a</sup>

Entry	Catalyst	Substrate	Time/T (°C)	Conv. (%)	Product <sup>d</sup>
1	$[1][B(C_6F_5)_4]$	1-hexyne	5 min/RT	98%	3
2	$[2][B(C_6F_5)_4]$	1-hexyne	7 days/RT	20%	3
3	$[1][B(C_6F_5)_4]$	4-phenylbutyne	5 min/RT	100%	4
4	$[2][B(C_6F_5)_4]$	4-Phenylbutyne	45 h/RT	100%	4
5	$[1][B(C_6F_5)_4]$	phenylacetylene	30 min/RT	100%	5
6	$[2][B(C_6F_5)_4]$	phenylacetylene	40 h/90 °C	100%	5
7	$[1][B(C_6F_5)_4]$	benzaldehyde	50 min/RT	90%	6
8	$[2][B(C_6F_5)_4]$	benzaldehyde	5 h/70 °C	90%	6
9	$[1][B(C_6F_5)_4]^b$	$CO_2^c$	41 h/90 °C	43%	MeOSiEt <sub>3</sub>
10	$[2][B(C_6F_5)_4]^b$	$CO_2^c$	41 h/90 °C	15%	MeOSiEt <sub>3</sub>

<sup>a</sup> Conditions: NMR-scale reactions, 5% mol of catalyst vs. silane (HSiEt<sub>3</sub>), solvent =  $C_6D_5Br$ . <sup>b</sup> 10% mol catalyst was used. <sup>c</sup> 1.5 atm of CO<sub>2</sub>. <sup>d</sup> hydrosilylation products **3–6** (Schemes 2 and 3) and MeOSiEt<sub>3</sub> were identified from NMR, GC–MS data and comparison with literature.

$$R \longrightarrow H \rightarrow SiEt_{3} \xrightarrow{[1-2][B(C_{6}F_{5})_{4}]} \qquad R \xrightarrow{SiEt_{3}} 3, R = nBu$$

$$H \longrightarrow H \rightarrow SiEt_{3} \xrightarrow{(5\% \text{ mol})} F \xrightarrow{H} \xrightarrow{SiEt_{3}} 5, R = PhCH_{2}CH_{2}$$

**Scheme 2.** Alkyne hydrosilylation catalyzed by [1–2][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



Scheme 3. Hydrosilylation of benzaldehyde and CO<sub>2</sub> catalyzed by [1-2][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

#### 4. Experimental section

# 4.1. Material, reagents and experimental methods

All work was performed under N<sub>2</sub> 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<sub>2</sub>, 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<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>D<sub>5</sub>Br as internal reference for <sup>1</sup>H ( $\delta$  of the most downfield signal = 7.16, 7.30, 5.32, 7.26 ppm) and  ${}^{13}C{}^{1}H{}(\delta \text{ of the most downfield signal = 128.39},$ 130.89, 53.84, 77.23 ppm). IR spectra were recorded on an alpha ATR spectrometer from Brucker Optics and analyzed with OPUS software. AlMe<sub>3</sub>, GaMe<sub>3</sub>, [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were obtained from Strem Chemicals Inc. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was obtained from TCI Europe and recrystallized from cold pentane prior to use. The M-NHC adducts (IDipp)AlMe<sub>3</sub>, (IDipp)GaMe<sub>3</sub> were prepared according to a literature procedure [15]. All other chemicals were purchased from Merck Corp. All olefinic, alkyne and carbonyl chemicals were dried over molecular sieves (4 Å) for a least 24 h prior to use. GC-MS analysis was conducted on a GC System 7820A (G4320) connected to a MSD block 5977E (G7036A) using Agilent High Resolution Gas Chromatography Column HP-5MS UI, 30 m, 0.25 mm, 0.25 µm.

# 4.2. Synthesis and characterisation of the Al and Ga complexes

# 4.2.1. $[(IDipp)AlMe_2][B(C_6F_5)_4]([1][B(C_6F_5)_4])$

To a solution of (IDipp)AlMe<sub>3</sub> (100 mg, 216.6  $\mu$ mol) in PhBr (1.5 mL) was added dropwise a stirring solution of [CPh<sub>3</sub>][B

(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (199.78 mg, 216,6 µmol) in PhBr (1.5 mL) at 25 °C giving a colorless solution at the end of the addition. The solvent was then immediately removed in vacuo and the oily residue triturated with pentane (3x5 mL) to obtain salt ( $[1][B(C_6F_5)_4]$ ) as an analytically pure white powder (96% yield). X-ray quality single crystals of  $[1][B(C_6F_5)_4]$  were grown at -35 °C by layering pentane over a PhBr solution of  $[1][B(C_6F_5)_4]$ . Anal. Calcd. for  $C_{53}H_{43}AlBF_{20}N_2$ : N, 2.49; C, 56.55; H, 3.85. Found: N, 2.47; C, 56.55; H, 3.81. <sup>1</sup>H NMR (400 MHz,  $C_6D_5Br$ ):  $\delta$  (ppm) 7.38 (t, J = 7.6 Hz, 2H, CH-Ar), 7.16 (d, J = 7.8 Hz, 4H, CH-Ar), 7.02 (s, 2H, NCHCHN), 2.32 (hept, J = 6.8 Hz, 4H, CH-<sup>i</sup>Pr), 1.20 (d, J = 6.7 Hz, 12H, CH<sub>3</sub>- <sup>i</sup>Pr), 1.01 (d, J = 6.9 Hz, 12H, CH<sub>3</sub>- <sup>i</sup>Pr), -1.06 (s, 6H, AlMe). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>5</sub>Br): δ (ppm) 163.05 (C<sub>carbene</sub>), 148.29 (dm,  $J_{CF}$  = 237.9 Hz, o-C<sub>6</sub>F<sub>5</sub>), 144.86 (C-Ar), 138.07 (dm,  $J_{CF}$  = 238.3 Hz,  $p-C_6F_5$ ), 136.18 (dm,  $J_{CF}$  = 239.1 Hz,  $m-C_6F_5$ ), 132.26 ( $C_{ipso}$ ), 131.44 (CH-Ar), 124.62 (CH-Ar), 121.97 (NCHCHN), 28.62 (CH-<sup>i</sup>Pr), 25.20 (CH<sub>3</sub>-<sup>i</sup>Pr), 22.01 (CH<sub>3</sub>-<sup>i</sup>Pr), -8.45 (Al(Me)<sub>2</sub>). <sup>19</sup>F NMR (282 MHz,  $C_6D_5Br$ ):  $\delta$  (ppm) -131.41 (d,  $J_{FF}$  = 11.7 Hz, 8F, o-F), -161.87 (t,  $J_{FF}$  = 21.0 Hz, 4F, p-F), -165.68 (t,  $J_{FF}$  = 18.8 Hz, 8F, m-F).

# 4.2.2. $[(IDipp)GaMe_2][B(C_6F_5)_4]([2][B(C_6F_5)_4])$

To a solution of (IDipp)GaMe3 (100 mg, 198.2 µmol) in PhBr (1.5 mL) was added dropwise a stirring solution of [CPh<sub>3</sub>][B (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (182.6 mg, 198.2 µmol) in PhBr (1.5 mL) at 25 °C giving a colorless solution. The solvent was then immediately removed *in vacuo* and the oily residue triturated with pentane (3x5 mL) to obtain salt  $([\mathbf{2}][B(C_6F_5)_4])$  as an analytically pure white powder (98% yield). Anal. Calcd. for C<sub>53</sub>H<sub>43</sub>GaBF<sub>20</sub>N<sub>2</sub>: N, 2.40; C, 54.48; H, 3.71. Found: N, 2.40; C, 54.53; H, 3.88. <sup>1</sup>H NMR (400 MHz,  $C_6D_5Br$ ):  $\delta$  (ppm) 7.36 (t, J = 7.8 Hz, 2H, CH-Ar), 7.16 (d, J = 7.7 Hz, 4H, CH-Ar), 6.95 (s, 2H, NCHCHN), 2.25 (hept, I = 6.9 Hz, 4H, CH-<sup>i</sup>Pr), 1.06 (d, I = 6.6 Hz, 12H, CH<sub>3</sub>- <sup>i</sup>Pr), 1.02 (d, J = 6.9 Hz, 12H, CH<sub>3</sub>- <sup>i</sup>Pr), -0.59 (s, 6H, Ga(Me)<sub>2</sub>). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>5</sub>Br):  $\delta$  (ppm) 164.45 (C<sub>carbene</sub>), 148.26 (dm,  $J_{CF}$  = 239.9 Hz, o-C<sub>6</sub>F<sub>5</sub>), 144.38 (C-Ar), 133.13 (dm,  $J_{CF}$  = 230.9 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.11 (dm, *J*<sub>CF</sub> = 239.5 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 131.30 (C<sub>*ipso*</sub>), 131.19 (CH-Ar), 124.96 (CH-Ar), 121.97 (NCHCHN), 28.62 (CH-<sup>i</sup>Pr), 24.54 (CH<sub>3</sub>-<sup>i</sup>Pr), 22.94 (CH<sub>3</sub>-<sup>i</sup>Pr), -1.32 (Ga(Me)<sub>2</sub>). <sup>19</sup>F NMR (282 MHz,  $C_6D_5Br$ ):  $\delta$  (ppm) -131.38 (d,  $J_{FF}$  = 10.7 Hz, 8F, o-F), -161.87 (t,  $J_{FF}$  = 21.1 Hz, 4F, p-F), -165.69 (t,  $J_{FF}$  = 18.8 Hz, 8F, m-F).

### 4.3. Alkene/alkyne hydrosilylation catalysis data

#### 4.3.1. General procedure

A J-Young NMR tube was charged with a solution of the appropriate catalyst  $[1-2][B(C_6F_5)_4]$  (4.4 µmol) in  $C_6D_5Br$  (0.5 mL), the alkene/alkyne (20 equiv vs. catalyst) and HSiEt<sub>3</sub> (20 equiv vs. catalyst). The reaction was monitored by <sup>1</sup>H NMR spectroscopy, allowing the idenfication of products on the basis of literature data. After completion of the reaction, the volatiles were removed under

vacuum for 1 h and the residue extracted with pentane. Further evaporation led to the desired NMR-pure hydrosilated products. For 1-hexene hydrosilylation attempts, poly(1-hexene) oligomers were found to be the major reaction products from 1H NMR data and were further analyzed by GPC and MALDI-TOF spectrometry. For the alkyne hydrosilylation products, GC–MS analysis confirmed their identity.

# 4.3.2. Attempted 1-hexene hydrosilylation by $[1-2][B(C_6F_5)_4]$ (5% mol)

In the presence of 1-hexene and  $HSiEt_3$  (20 equiv of each), cation [1][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5% mol.) is unreactive at room temperature for 48 h. The oligomerization of 1-hexene occurred upon heating (65 °C, C<sub>6</sub>D<sub>5</sub>Br, quantitative conv. of 1-hexene after 3 and 10 days for [1][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [2][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], respectively) as deduced from <sup>1</sup>H NMR data.[26] Isolation of the products and subsequent GPC and MALDI-TOF analysis confirmed the formation of oligomers.

# 4.3.3. Alkyne hydrosilylation catalyzed by $[1][(B(C_6F_5)_4] (5\% mol)]$

In the presence of 1-hexyne and HSiEt<sub>3</sub> (20 equiv of each), the Al salt [1][(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5% mol.) catalyzes the E-selective hydrosilylation reaction of 1-hexyne/4-phenylbutyne/phenylacetylene at room temperature (C<sub>6</sub>D<sub>5</sub>Br) to afford the corresponding vinyl silane mono-hydrosilylated Z-selective products **3–5**. **Data for 3**: 98% conv. within 5 min, <sup>1</sup>H NMR data in agreement with literature data [27], GC/MS: t<sub>R</sub> = 4.311 min (100%), *m/z* 198.20, triethyl (hexyl-1-en-1-yl)silane). **Data for 4**: 100% conv. within 5 min, <sup>1</sup>H NMR data [28], GC/MS: t<sub>R</sub> = 6.248 min (100%), *m/z* = 246.10, (Z)-triethyl(4-phenylbut-1-enyl)silane. **Data for 5**: 100% conv. within 30 h, <sup>1</sup>H NMR data in line with literature data [29], GC/MS: t<sub>R</sub> = 5.373 min (100%), *m/z* = 218.20, (E)-triethyl (styryl)silane.

### 4.3.4. 1-Hexyne hydrosilylation catalyzed by $[2][(B(C_6F_5)_4]]$

In the presence of 1-hexyne/4-phenylbutyne/phenylacetylene and  $HSiEt_3$  (20 equiv of each), the Ga salt [**2**][(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5% mol.) is unreactive at room temperature but slowly catalyzes the *trans*-hydrosilylation of 1-hexyne to selectively afford mono-hydrosilylation over an extended time to afford the Z-product **3** (20% conv. after 7 days).

# 4.3.5. Benzaldehyde hydrosilylation catalyzed by $[1-2][B(C_6F_5)_4]$

In the presence of benzaldehyde and HSiEt<sub>3</sub> (20 equiv of each), the Al species [**1**][(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5% mol.) fast catalyzes benzaldehyde hydrosilylation at room temperature (C<sub>6</sub>D<sub>5</sub>Br, 90% conv., within 50 min) to afford (benzyloxy)silane **6**, while the Ga analogue [**2**] [(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5% mol.) led to 90% conversion of 20 equiv of benzaldehyde/HSiEt<sub>3</sub> to **6** within 50 min at 70 °C. Product **6** was identified by <sup>1</sup>H NMR spectroscopy (data match literature data) [30] and its formation was confirmed by GC–MS analysis. GC/MS: t<sub>R</sub> = 5.227 min (100%), *m/z* = 220.10, (benzyloxy)silane.

CO<sub>2</sub> hydrosilylation catalyzed by  $[1-2][B(C_6F_5)_4]$ . A J-Young valve NMR tube was charged with a solution of catalyst  $[1-2][(B(C_6F_5)_4]$  in C<sub>6</sub>D<sub>5</sub>Br (0.5 mL). The desired amount of HSiEt<sub>3</sub> (10 equiv *vs.* catalyst) was then added. The mixture was degassed through vacuum and charged with CO<sub>2</sub> to deliver *ca* 1.5 atm of CO<sub>2</sub> at room temperature. The temperature of the reaction was then increased to 90 °C in a pre-heated oil bath and the reaction was monitored by <sup>1</sup>H NMR spectroscopy. Under these conditions, a slow but selective formation of the CO<sub>2</sub> hydrosilylation product MeOSiEt<sub>3</sub> was identified by <sup>1</sup>H NMR [43% and 15% conversion (*vs.* HSiEt<sub>3</sub>) to MeOSiEt<sub>3</sub> with catalyst [1][(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [2][(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], respectively).

# **CRediT authorship contribution statement**

**Anaëlle Bolley:** Data curation, Methodology. **David Specklin:** Data curation, Methodology. **Samuel Dagorne:** Supervision, Writing - review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114956.

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