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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)AlMe₂(PhBr)]⁺ (**[1]**⁺, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and (IDipp)GaMe₂]⁺ (**[2]**⁺), were prepared and structurally characterized as B(C₆F₅)₄[−] salts *via* ionization of the corresponding neutral precursors (IDipp)MMe₃ (M = Al, Ga) with [Ph₃C][B(C₆F₅)₄] in PhBr at room temperature. Both **[1]**[B(C₆F₅)₄] and **[2]**[B(C₆F₅)₄] salt were isolated in high yield and their solid state structures established through X-ray crystallographic studies. Cations **[1]**⁺ and **[2]**⁺, 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 CO₂ using HSiEt₃ 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 PhCH₂OSiEt₃ (**6**). Cations **[1]**⁺ and **[2]**⁺ also slowly catalyze CO₂ hydrosilylation with the selective formation of the methanol-equivalent MeOSiEt₃.

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*-/*O*-based 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_2^+ and AlBr_2^+ also catalyze CO_2 hydrosilylation and carbonyl-olefin metathesis, respectively, further illustrating the potential of low-coordinate Al cations in catalysis [7,8]. Three-coordinate Al cations of the type $(\text{NacNac})\text{Al-R}^+$ ($\text{R} = \text{H}$, 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 σ -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 ($\text{M} = \text{Al}$, Ga , In) [11]. Early examples of Al-NHC species of the type $(\text{NHC})\text{AlX}_3$ 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 $[(\text{NHC})_2\text{AlH}_2]^+$, $[(\text{NHC})\text{AlH}]^+$, $[(\text{NHC})_2\text{Al-H}]^{2+}$ and $[(\text{NHC})\text{AlH}_2]_2^{2+}$ were recently characterized [13,14]. We also showed

that four-coordinate cations of the type $(\text{NHC})\text{MR}_2(\text{L})^+$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$; $\text{L} = \text{Et}_2\text{O}, \text{THF}$) 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 $(\text{NHC})\text{MR}_2^+$ ($\text{M} = \text{Al}, \text{Ga}$) 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 $(\text{NHC})\text{AlMe}_2^+$ and $(\text{NHC})\text{GaMe}_2^+$. Such strong electrophiles were exploited in aldehyde, alkyne and CO_2 hydrosilylation catalysis, as also discussed herein.

Results – Discussion

Synthesis and structure of the Al-NHC and Ga-NHC cations $(\text{IDipp})\text{MMe}_2^+$ ($\text{M} = \text{Al}, \text{Ga}$). $[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\mathbf{2}][\text{B}(\text{C}_6\text{F}_5)_4]$. Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ were prepared *via* a methide abstraction reaction of the corresponding neutral precursors $(\text{IDipp})\text{AlMe}_3$ and $(\text{IDipp})\text{GaMe}_3$ ($\text{IDipp} =$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [15], a methodology well-established in the literature [2,3]. Thus, the ionization reaction of $(\text{IDipp})\text{MMe}_3$ ($\text{M} = \text{Al}, \text{Ga}$) and 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (PhBr , room temperature) led to the quantitative formation of cations $[(\text{IDipp})\text{AlMe}_2]^+$ ($\mathbf{1}^+$) and $[(\text{IDipp})\text{GaMe}_2]^+$ ($\mathbf{2}^+$), respectively, as $\text{B}(\text{C}_6\text{F}_5)_4^-$ salts (Scheme 1), as deduced from NMR data. Both cations, $[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\mathbf{2}][\text{B}(\text{C}_6\text{F}_5)_4]$, were isolated in high yield as analytically pure colorless solids. In solution, both salts are unstable in CH_2Cl_2 and decomposes within minutes at room temperature to unknown species, likely reflecting the strong Lewis acidity of cations $\mathbf{1}^+$ and $\mathbf{2}^+$ [17]. In contrast, the earlier reported $[(\text{NHC})\text{MR}_2(\text{L})]^+$ ($\text{M} = \text{Al}, \text{Ga}$; $\text{L} = \text{Et}_2\text{O}, \text{THF}$) cations are stable for days in CH_2Cl_2 confirming that Lewis bases such as Et_2O and THF significantly quench the Lewis acidity of the $(\text{NHC})\text{MR}_2^+$ ($\text{M} = \text{Al}, \text{Ga}$) moiety.

Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ are however stable for days in PhBr under inert atmosphere. The ^1H , ^{13}C and ^{19}F NMR data for $[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\mathbf{2}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{C}_6\text{D}_5\text{Br}$, 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 ^1H NMR resonances include: 1) a significantly downfield shifted ^1H NMR chemical shift for the *H*-C4/C5 NHC resonance (δ 7.02 ppm) vs. that in neutral precursor (IDipp)AlMe₃ (δ 6.58 ppm), in line with NHC coordination with the more electrophilic $[\text{AlR}_2]^+$ moiety; 2) an upfield shifted C_{carbene} ^{13}C NMR signal (δ 163.0 vs. 178.3 ppm in (IDipp)AlMe₃) reflecting an enhanced Lewis acidity of the Al(III) center in cation $\mathbf{1}^+$.

Scheme 1. Synthesis of the NHC-supported Al(III) and Ga(III) species $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$

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 $[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4]$, crystallized from a PhBr/pentane solution, was confirmed through X-ray crystallographic

analysis. Salt $[1][B(C_6F_5)_4]$ crystallizes as discrete Al-PhBr cationic adducts and $[B(C_6F_5)_4]^-$ anions with no cation/anion interactions (Figure S7, SI). As shown in Figure 1, the Al cation $[1-PhBr]^+$ consists of a $[AlMe_2]^+$ moiety stabilized by one IDipp carbene and the coordination of PhBr through the Br atom. To our knowledge, $[1-PhBr]^+$ 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^+ . 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 $[1-PhBr]^+$. PhBr coordination causes a slight pyramidalization of the geometry around the Al(III) center the $[(IDipp)AlMe_2]^+$, as reflected by the sum of C-Al-C bond angles (around 351°). The Al-C_{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)AlMe₃ (2.103(3) Å) [20].

Figure 1. Molecular structure of the Al cation $[1]^+$ (ORTEP view; ellipsoids enclose 50% electronic density) with selected atom labeling for clarity. The hydrogen atoms are omitted for clarity.

The molecular structure of the Ga(III) salt $[2][B(C_6F_5)_4]$, crystallized from PhBr/toluene, was also confirmed through X-ray crystallographic analysis, and consists of discrete $[2]^+$ and $[B(C_6F_5)_4]^-$ ions with no cation/anion interactions (Figure S8, SI). As depicted in Figure 2, cation $[2]^+$ 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_{NHC} bond distance (2.018(3) Å) than in (IDipp)GaMe₃ precursor (2.105(4) Å) [20]. The absence of PhBr coordination to the Ga(III) center in $[2]^+$ presumably indicates the lower Lewis acidity of Ga(III) vs. Al(III).

Figure 1. Molecular structure of the Ga cation $[2]^+$ (ORTEP view; ellipsoids enclose 50% electronic density) with selected atom labeling for clarity. The hydrogen atoms are omitted for clarity.

Cations $[1]^+$ and $[2]^+$ immediately reacted with 1 equiv Et₂O or THF (C₆D₅Br, room to form the corresponding four-coordinate cationic adducts $[(NHC)MR_2(L)]^+$ (M = Al, Ga; L = Et₂O, 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]. Accordingly to these measurements, the Lewis acidity of the Al cation $[1]^+$ is similar to that of B(C₆F₅)₃, a

landmark Lewis acid ($\Delta\delta^{31}\text{P}$ ($\text{C}_6\text{D}_5\text{Br}$) = 76.2 and 76.6 ppm for $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\mathbf{1}]^+$, respectively). The Ga cation $[\mathbf{2}]^+$ appears to be slightly less Lewis acidic ($\Delta\delta^{31}\text{P}$ ($\text{C}_6\text{D}_5\text{Br}$) = 73.2 ppm), in line with other structural data.

Table 1. Lewis acidity assessment of salt $[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\mathbf{2}][\text{B}(\text{C}_6\text{F}_5)_4]$ via the Gutmann-Beckett method^a

	POEt_3	$\text{B}(\text{C}_6\text{F}_5)_3 + 1$ equiv POEt_3	$[\mathbf{1}][\text{B}(\text{C}_6\text{F}_5)_4] + 1$ equiv POEt_3	$[\mathbf{2}][\text{B}(\text{C}_6\text{F}_5)_4] + 1$ equiv POEt_3
^{31}P NMR ($\text{C}_6\text{D}_5\text{Br}$) $\delta(\text{ppm})$	46.8	76.2	76.6	73.2

^a The ^{31}P NMR chemical shift difference between the $\text{Et}_3\text{P}=\text{O}$ Lewis adduct and free $\text{Et}_3\text{P}=\text{O}$ allows an estimation of Lewis acidity [21]. The ^{31}P NMR measurements were done in $\text{C}_6\text{D}_5\text{Br}$ at RT.

Alkene/alkyne hydrosilylation catalysis mediated by $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$. The Lewis acidic Al and Ga salts $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$ were initially tested in 1-hexene hydrosilylation. As monitored by ^1H NMR, no reaction was observed at room temperature in $\text{C}_6\text{D}_5\text{Br}$ between $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$ (5% mol) and a 1/1 1-hexene/ HSiEt_3 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_3 . 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 $[\mathbf{1}]^+$ was found to be an extremely efficient and selective for alkyne hydrosilylation, allowing the fast and quantitative *trans*-hydrosilylation of 1-hexyne, 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 $[\mathbf{1}]^+$ retains its integrity as the catalysis proceeds, which is consistent with $[\mathbf{1}]^+$ solely acting as a Lewis acid.

Al-based alkyne hydrosilylation catalysis have thus far been restricted to the use of AlCl_3 as catalyst, yet requiring a much higher catalytic loading (typically 20% mol) and an extremely careful AlCl_3 purification prior to catalysis [23].

Scheme 2. Alkyne hydrosilylation catalyzed by $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$

The present Al-catalyzed alkyne hydrosilylation likely occur in a similar way to that observed with AlCl_3 with 1,2 *anti*-addition of $\text{H}-\text{SiEt}_3$ to the C–C triple bond [23a]. As a comparison, the less Lewis acidic Ga cation $[\mathbf{2}]^+$ 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**.

Benzaldehyde and CO_2 hydrosilylation catalysis mediated by $[\mathbf{1-2}][\text{B}(\text{C}_6\text{F}_5)_4]$. The potential of Al and Ga cations $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ as Lewis acidic catalysts for the hydrosilylation of carbonyl substrates was also evaluated. Thus, $[\mathbf{1}]^+$ (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_3 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 $[\mathbf{2}]^+$ 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].

Scheme 3. Hydrosilylation of benzaldehyde and CO₂ catalyzed by [1-2][B(C₆F₅)₄]

Despite being a challenging carbonyl substrate for activation/functionalization, CO₂ was recently shown to be reduced to methanol-equivalent MeOSiR₃ products and/or methane by Lewis acid-promoted hydrosilylation, primarily using Al- and Zn-based cations as strong electrophiles [7,25]. Salt [1-2][B(C₆F₅)₄] were thus probed as CO₂ hydrosilylation catalysts and exhibited moderate performances (entries 9 and 10, Table 2). Thus, in the presence of CO₂ (1.5 atm) and HSiEt₃ (10 equiv vs. catalyst), Al cation [1]⁺ slowly but selectively hydrosilylates CO₂ to methanol-equivalent MeOSiEt₃ (C₆D₅Br, 90 °C, 41 h, 43% conversion to MeOSiEt₃), 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 (C₆D₅Br, 90 °C, 41 h, 15% conversion to MeOSiEt₃). For both catalysts [1]⁺ and [2]⁺, MeOSiEt₃ was the only observed product by ¹H NMR, thus with no NMR detection of the first and second hydrosilylation products, formate HCO₂SiEt₃ and ketal Et₃SiO-CH₂-OSiEt₃, respectively, as the CO₂ hydrosilylation proceeds. The latter is in line with the initial CO₂ activation/functionalization being rate-limiting, as has been observed for other Lewis acid-type CO₂ hydrosilylation catalysts [7,25], and fast consumption of HCO₂SiEt₃ to Et₃SiO-CH₂-OSiEt₃ and eventually MeOSiEt₃.

Table 2. Alkyne, benzaldehyde and CO₂ hydrosilylation catalysis results using [1-2][B(C₆F₅)₄] as catalysts and HSiEt₃ as an hydrosilane source^a

Entry	Catalyst	Substrate	Time/T (°C)	Conv. (%)	Product ^d

1	[1] [B(C ₆ F ₅) ₄]	1-hexyne	5 min/RT	98%	3
2	[2] [B(C ₆ F ₅) ₄]	1-hexyne	7 days/RT	20%	3
3	[1] [B(C ₆ F ₅) ₄]	4-phenylbutyne	5 min/RT	100%	4
4	[2] [B(C ₆ F ₅) ₄]	4-Phenylbutyne	45 h/RT	100%	4
5	[1] [B(C ₆ F ₅) ₄]	phenylacetylene	30 min/RT	100%	5
6	[2] [B(C ₆ F ₅) ₄]	phenylacetylene	40 h/90 °C	100%	5
7	[1] [B(C ₆ F ₅) ₄]	benzaldehyde	50 min/RT	90%	6
8	[2] [B(C ₆ F ₅) ₄]	benzaldehyde	5 h/70 °C	90%	6
9	[1] [B(C ₆ F ₅) ₄] ^b	CO ₂ ^c	41 h/90 °C	43%	MeOSiEt ₃
10	[2] [B(C ₆ F ₅) ₄] ^b	CO ₂ ^c	41 h/90 °C	15%	MeOSiEt ₃

^a Conditions: NMR-scale reactions, 5% mol of catalyst vs. silane (HSiEt₃), solvent = C₆D₅Br.

^b 10% mol catalyst was used. ^c 1.5 atm of CO₂. ^d hydrosilylation products **3-6** (Schemes 2 and 3) and MeOSiEt₃ were identified from NMR, GC-MS data and comparison with literature.

Conclusion

The present study showed that NHC-supported Al(III) and Ga(III) alkyl cations of the type [(NHC)AlMe₂(PhBr)]⁺ and [(NHC)GaMe₂]⁺ may be readily prepared as thermally stable yet strongly electrophilic species. Cations **[1]**⁺ and **[2]**⁺, 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 CO₂. As a comparison, it may be noted that robust four-coordinate [(NHC)MR₂(L)]⁺ (M = Al, Ga; L = Et₂O, 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]**⁺ is significantly more active than its Ga analogue **[2]**⁺, while both cations display identical selectivities across all hydrosilylations. All hydrosilylation catalysis data agree with Lewis acid-mediated processes mediated by **[1]**⁺ and **[2]**⁺.

Experimental Section

Material, reagents and experimental methods. All work was performed under N₂ atmosphere using standard glove box techniques. Solvents were stored over 4 Å molecular sieves and were freshly distilled under argon from sodium-benzophenone or CaH₂, 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 C₆D₆, C₆D₅Br as internal reference for ¹H (δ of the most downfield signal = 7.16, 7.30, 5.32, 7.26 ppm) and ¹³C{¹H} (δ of the most downfield signal = 128.39, 130.89, 53.84, 77.23 ppm). IR spectra were recorded on an alpha ATR spectrometer from Bruker Optics and analyzed with OPUS software. AlMe₃, GaMe₃, [CPh₃][B(C₆F₅)₄] were obtained from Strem Chemicals Inc. B(C₆F₅)₃ was obtained from TCI Europe and recrystallized from cold pentane prior to use. The M-NHC adducts (IDipp)AlMe₃, (IDipp)GaMe₃ 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.

Synthesis and characterisation of the Al and Ga complexes

[(IDipp)AlMe₂][B(C₆F₅)₄] ([1][B(C₆F₅)₄]). To a solution of (IDipp)AlMe₃ (100 mg, 216.6 μmol) in PhBr (1.5 mL) was added dropwise a stirring solution of [CPh₃][B(C₆F₅)₄] (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(C₆F₅)₄]) as an analytically pure white powder (96% yield). X-ray quality single crystals of **[1]**[B(C₆F₅)₄] were grown at -35 °C by layering pentane over a PhBr solution of **[1]**[B(C₆F₅)₄]. Anal. Calcd. for C₅₃H₄₃AlBF₂₀N₂: N, 2.49; C, 56.55; H, 3.85. Found: N, 2.47; C, 56.55; H, 3.81. ¹H NMR (400 MHz, C₆D₅Br): δ (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-ⁱPr), 1.20 (d, *J* = 6.7 Hz, 12H, CH₃-ⁱPr), 1.01 (d, *J* = 6.9 Hz, 12H, CH₃-ⁱPr), -1.06 (s, 6H, AlMe). ¹³C NMR (126 MHz, C₆D₅Br): δ (ppm) 163.05 (C_{carbene}), 148.29 (dm, *J*_{CF}=237.9 Hz, *o*-C₆F₅), 144.86 (C-Ar), 138.07 (dm, *J*_{CF}=238.3 Hz, *p*-C₆F₅), 136.18 (dm, *J*_{CF}=239.1 Hz, *m*-C₆F₅), 132.26 (C_{ipso}), 131.44 (CH-Ar), 124.62 (CH-Ar), 121.97 (NCHCHN), 28.62 (CH-ⁱPr), 25.20 (CH₃-ⁱPr), 22.01 (CH₃-ⁱPr), -8.45 (Al(Me)₂). ¹⁹F NMR (282 MHz, C₆D₅Br): δ (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).

[(IDipp)GaMe₂][B(C₆F₅)₄] ([2]**[B(C₆F₅)₄]).** To a solution of (IDipp)GaMe₃ (100 mg, 198.2 μmol) in PhBr (1.5 mL) was added dropwise a stirring solution of [CPh₃][B(C₆F₅)₄] (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 (**[2]**[B(C₆F₅)₄]) as an analytically pure white powder (98% yield). Anal. Calcd. for C₅₃H₄₃GaBF₂₀N₂: N, 2.40; C, 54.48; H, 3.71. Found: N, 2.40; C, 54.53; H, 3.88. ¹H NMR (400 MHz, C₆D₅Br): δ (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, *J*=6.9 Hz, 4H, CH-ⁱPr), 1.06 (d, *J*=6.6 Hz, 12H, CH₃-ⁱPr), 1.02 (d, *J*=6.9 Hz, 12H, CH₃-ⁱPr), -0.59 (s, 6H, Ga(Me)₂). ¹³C NMR (126 MHz, C₆D₅Br): δ (ppm) 164.45 (C_{carbene}), 148.26 (dm, *J*_{CF}=239.9 Hz, *o*-C₆F₅), 144.38 (C-Ar), 133.13 (dm, *J*_{CF}=230.9 Hz, *p*-C₆F₅), 136.11 (dm, *J*_{CF}=239.5 Hz, *m*-C₆F₅), 131.30 (C_{ipso}), 131.19 (CH-Ar), 124.96 (CH-Ar), 121.97 (NCHCHN), 28.62 (CH-ⁱPr), 24.54 (CH₃-ⁱPr), 22.94 (CH₃-ⁱPr), -1.32

(Ga(Me)₂). ¹⁹F NMR (282 MHz, C₆D₅Br): δ (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).

Alkene/alkyne hydrosilylation catalysis data

General procedure. A J-Young NMR tube was charged with a solution of the appropriate catalyst [**1-2**][B(C₆F₅)₄] (4.4 μmol) in C₆D₅Br (0.5 mL), the alkene/alkyne (20 equiv *vs.* catalyst) and HSiEt₃ (20 equiv *vs.* catalyst). The reaction was monitored by ¹H NMR spectroscopy, allowing the identification 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.

Attempted 1-hexene hydrosilylation by [1-2**][B(C₆F₅)₄] (5% mol).** In the presence of 1-hexene and HSiEt₃ (20 equiv of each), cation [**1**][B(C₆F₅)₄] (5% mol.) is unreactive at room temperature for 48 h. The oligomerization of 1-hexene occurred upon heating (65 °C, C₆D₅Br, quantitative conv. of 1-hexene after 3 and 10 days for [**1**][B(C₆F₅)₄] and [**2**][B(C₆F₅)₄], respectively) as deduced from ¹H NMR data.²⁶ Isolation of the products and subsequent GPC and MALDI-TOF analysis confirmed the formation of oligomers.

Alkyne hydrosilylation catalyzed by [1**][B(C₆F₅)₄] (5% mol).** In the presence of 1-hexyne and HSiEt₃ (20 equiv of each), the Al salt [**1**][B(C₆F₅)₄] (5% mol.) catalyzes the E-selective hydrosilylation reaction of 1-hexyne/4-phenylbutyne/phenylacetylene at room temperature (C₆D₅Br) to afford the corresponding vinyl silane mono-hydrosilylated Z-selective products

3-5. Data for 3: 98% conv. within 5 min, ^1H NMR data in agreement with literature data,²⁷ GC/MS: $t_{\text{R}} = 4.311$ min (100%), m/z 198.20, triethyl(hexyl-1-en-1-yl)silane). **Data for 4:** 100% conv. within 5 min, ^1H NMR data in line literature data,²⁸ GC/MS: $t_{\text{R}} = 6.248$ min (100%), $m/z = 246.10$, (Z)-triethyl(4-phenylbut-1-enyl)silane. **Data for 5:** 100% conv. within 30 h, ^1H NMR data in line with literature data,²⁹ GC/MS: $t_{\text{R}} = 5.373$ min (100%), $m/z = 218.20$, (E)-triethyl(styryl)silane.

1-Hexyne hydrosilylation catalyzed by [2][(B(C₆F₅)₄)]. In the presence of 1-hexyne/4-phenylbutyne/phenylacetylene and HSiEt₃ (20 equiv of each), the Ga salt [2][(B(C₆F₅)₄)] (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).

Benzaldehyde hydrosilylation catalyzed by [1-2][(B(C₆F₅)₄)]. In the presence of benzaldehyde and HSiEt₃ (20 equiv of each), the Al species [1][(B(C₆F₅)₄)] (5% mol.) fast catalyzes benzaldehyde hydrosilylation at room temperature (C₆D₅Br, 90% conv., within 50 min) to afford (benzyloxy)silane **6**, while the Ga analogue [2][(B(C₆F₅)₄)] (5% mol.) led to 90% conversion of 20 equiv of benzaldehyde/HSiEt₃ to **6** within 50 min at 70 °C. Product **6** was identified by ^1H NMR spectroscopy (data match literature data)³⁰ and its formation was confirmed by GC-MS analysis. GC/MS: $t_{\text{R}} = 5.227$ min (100%), $m/z = 220.10$, (benzyloxy)silane.

CO₂ hydrosilylation catalyzed by [1-2][(B(C₆F₅)₄)]. A J-Young valve NMR tube was charged with a solution of catalyst [1-2][(B(C₆F₅)₄)] in C₆D₅Br (0.5 mL). The desired amount of HSiEt₃ (10 equiv vs. catalyst) was then added. The mixture was degassed through vacuum and

charged with CO₂ to deliver *ca* 1.5 atm of CO₂ 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 ¹H NMR spectroscopy. Under these conditions, a slow but selective formation of the CO₂ hydrosilylation product MeOSiEt₃ was identified by ¹H NMR [43% and 15% conversion (*vs.* HSiEt₃) to MeOSiEt₃ with catalyst **[1]**[(B(C₆F₅)₄] and **[2]**[(B(C₆F₅)₄], respectively).

CRedit authorship contribution statement

Anaëlle Bolley: Experimental work, Data curation, Methodology, Writing. **David Specklin:** Experimental work, Data curation, Methodology. **Samuel Dagorne:** Supervision, Writing.

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

CCDC 2041906 and 2041907 contain the supplementary crystallographic data for **[1]**[(B(C₆F₅)₄] and **[2]**[(B(C₆F₅)₄], respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. NMR spectra of compounds and catalytic runs are also included in supplementary data.

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