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# Structure, Stability, and Catalytic Activity of Fluorine-Bridged Complexes $\text{IPr}\cdot\text{GaCl}_2(\mu\text{-F})\text{EF}_{n-1}$ ( $\text{EF}_n^- = \text{SbF}_6^-, \text{PF}_6^-, \text{or } \text{BF}_4^-$ )

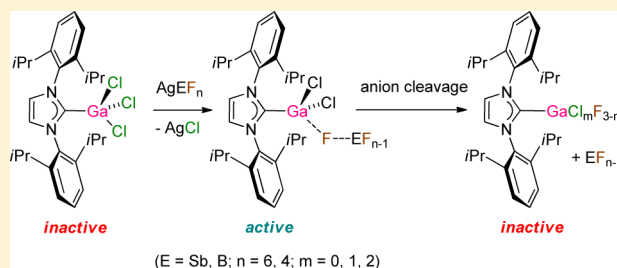
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## S Supporting Information

**ABSTRACT:** Fluorine-bridged NHC–gallium(III) complexes of the type  $\text{IPr}\cdot\text{GaCl}_2(\mu\text{-F})\text{EF}_{n-1}$  [ $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$ , and  $\text{EF}_n = \text{SbF}_6^-$  or  $\text{BF}_4^-$ ] have been synthesized and characterized in solution and in the solid state. The  $[\text{BF}_4]^-$  adduct readily decomposes into gallium fluorides of the type  $[\text{IPr}\cdot\text{GaCl}_m\text{F}_{3-m}]$  ( $m = 0, 1, \text{ or } 2$ ) with release of gaseous  $\text{BF}_3$ . These results corroborate the trend observed in  $\text{IPr}\cdot\text{GaCl}_3/\text{AgEF}_n$ -catalyzed reactions in which a strong anion effect exists.



## INTRODUCTION

It is now clearly established that weakly coordinating anions (WCAs)<sup>1</sup> are not always innocent bystanders in reactions catalyzed by cationic metal complexes.<sup>2</sup> The possible establishment of weakly covalent or noncovalent interactions between the WCA and the ligands, the metal, or the reacting substrate can dramatically affect the selectivity, notably the stereoselectivity.<sup>3</sup> This role of WCA in catalysis concerns not only chiral counterions but also simple and widely used anions such as  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ , etc.<sup>4</sup> Thus, knowing where the anion actually lies during the catalytic process is of prime importance.<sup>5</sup> The second issue concerns the compatibility between the cationic moiety and the anion. In fact, not every WCA is stable toward its cationic counterpart. The cleavage of WCAs (tetraarylbates or perfluoro anions) by transition metal cations is a well-documented topic.<sup>6–8</sup> On the other hand, the effect on catalysis of this decomposition, which might induce the inhibition of the active species or give rise to unexpected acidic compounds that become the real catalysts, has been rarely discussed.<sup>9</sup>

There is a clear trend in homogeneous catalysis to develop substitutes of the rare late transition metals, notably through the use of abundant main group elements.<sup>10</sup> For instance, it was shown that neutral gallium salts can mimic the reactivity of iridium-, gold-, platinum-, or other noble metal-based catalysts in some reactions involving the activation of C–C  $\pi$  bonds.<sup>11,12</sup> If cationic main group metal complexes are targeted, the issue of the compatibility between the strongly electrophilic metal center and the accompanying WCA arises. In the course of our work on gallium catalysis, we have been confronted by this issue. We have recently reported the first applications of cationic gallium complexes in molecular catalysis.<sup>13</sup> Species such as  $[\text{IPr}\cdot\text{GaCl}_2(\text{L})][\text{SbF}_6]$  [ $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$ , and  $\text{L} = 2,4,6\text{-trifluor-}$

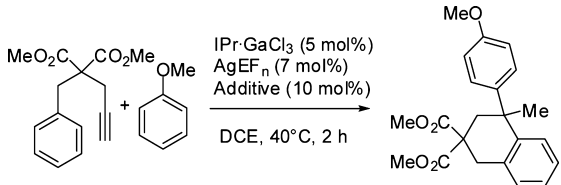
obenzonitrile] were used as  $\pi$ -Lewis acids for the activation of alkynes toward nucleophilic attack. To study the influence of the anion on selectivity, we decided to use  $\text{PF}_6^-$  and  $\text{BF}_4^-$  instead of  $\text{SbF}_6^-$ . We show herein that these two anions are easily cleaved under the catalytic conditions. Only a few examples of perfluoro anion cleavage have been reported in the main group series.<sup>14</sup> This study led us to characterize novel gallium F-bridged complexes of the type  $\text{IPr}\cdot\text{GaCl}_2(\mu\text{-F})\text{EF}_{n-1}$  ( $\text{EF}_n = \text{SbF}_6^-$  or  $\text{BF}_4^-$ ) and gallium fluorides.

## RESULTS AND DISCUSSION

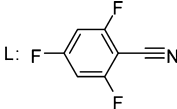
We recently reported<sup>13</sup> that a mixture of  $\text{IPr}\cdot\text{GaCl}_3$ <sup>35e</sup> and  $\text{AgSbF}_6$  efficiently catalyzes cycloisomerization/Friedel–Crafts tandem reactions such as the one shown in Table 1 (entry 1). After having rationalized the benefits of using the IPr or other carbon-based ligands in this chemistry,<sup>15</sup> we then decided to study the influence of the silver salt. The use of  $\text{AgPF}_6$  or  $\text{AgBF}_4$  instead of  $\text{AgSbF}_6$  resulted in a dramatic decrease in activity (entries 2 and 3).<sup>16</sup> Because neither  $\text{IPr}\cdot\text{GaCl}_3$  nor  $\text{AgSbF}_6$  can by itself promote this transformation, it is likely that chloride abstraction takes place to generate  $[\text{IPr}\cdot\text{GaCl}_2][\text{SbF}_6]$  as the active species. Thus, several hypotheses might explain the inactivity of the  $\text{IPr}\cdot\text{GaCl}_3/\text{AgPF}_6$  and  $\text{IPr}\cdot\text{GaCl}_3/\text{AgBF}_4$  systems. (i) The anion metathesis does not take place with  $\text{AgPF}_6$  or  $\text{AgBF}_4$ . (ii) The substitution of the anion of  $[\text{IPr}\cdot\text{GaCl}_2][\text{EF}_n]$  by the substrate does not take place when  $[\text{EF}_n]^- = [\text{PF}_6]^-$  or  $[\text{BF}_4]^-$ . (iii)  $[\text{IPr}\cdot\text{GaCl}_2][\text{EF}_n]$  decomposes into inactive species when  $[\text{EF}_n]^- = [\text{PF}_6]^-$  or  $[\text{BF}_4]^-$ . The first two hypotheses could be ruled out by additional experiments involving a Lewis base or an ammonium salt. When a catalytic amount of 2,4,6-trifluorobenzonitrile was used<sup>17</sup> in the reaction

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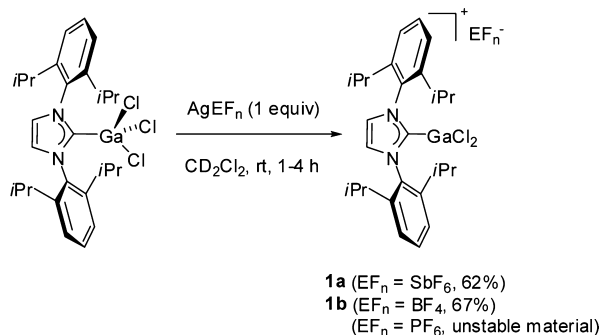
**Table 1.** Counterion Effect in Ga(III)-Catalyzed Cycloisomerization/Friedel–Crafts Tandem Reaction


entry	AgEF <sub>n</sub>	additive	GC conversion (%)
1	AgSbF <sub>6</sub>	none	99
2	AgPF <sub>6</sub>	none	2
3	AgBF <sub>4</sub>	none	trace
4	AgSbF <sub>6</sub>	L	97
5	AgPF <sub>6</sub>	L	54
6	AgBF <sub>4</sub>	L	1
7	AgSbF <sub>6</sub>	[ <i>n</i> Bu <sub>4</sub> N][SbF <sub>6</sub> ]	98
8	AgSbF <sub>6</sub>	[ <i>n</i> Bu <sub>4</sub> N][PF <sub>6</sub> ]	47
9	AgSbF <sub>6</sub>	[ <i>n</i> Bu <sub>4</sub> N][BF <sub>4</sub> ]	5
10	AgPF <sub>6</sub>	[ <i>n</i> Bu <sub>4</sub> N][SbF <sub>6</sub> ]	97
11	AgBF <sub>4</sub>	[ <i>n</i> Bu <sub>4</sub> N][SbF <sub>6</sub> ]	73

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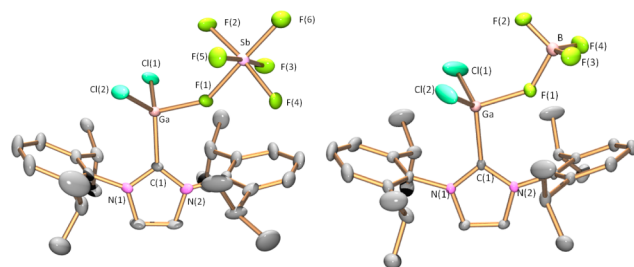
mixture, a significant improvement was observed with AgPF<sub>6</sub> (entry 5), but not with AgBF<sub>4</sub> (entry 6). Besides, the catalytic activity of the IPr-GaCl<sub>3</sub>/AgSbF<sub>6</sub> mixture could be strongly diminished in the presence of [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] (entry 8) and virtually shut down with [*n*Bu<sub>4</sub>N][BF<sub>4</sub>] (entry 9).<sup>18,19</sup> On the other hand, the IPr-GaCl<sub>3</sub>/AgPF<sub>6</sub> and, to a lesser extent, IPr-GaCl<sub>3</sub>/AgBF<sub>4</sub> systems became efficient when [*n*Bu<sub>4</sub>N][SbF<sub>6</sub>] was used as the additive (entries 10 and 11).<sup>20</sup> These control experiments suggest an efficient anion metathesis with each silver salt and rapid deactivation of [IPr-GaCl<sub>2</sub>][PF<sub>6</sub>] and especially [IPr-GaCl<sub>2</sub>][BF<sub>4</sub>]. The decay can be retarded by keeping the anion away from the coordination sphere of gallium using a neutral Lewis base or a compatible anion.

To gain evidence of the anion metathesis, we aimed to isolate the adducts formed upon treatment of IPr-GaCl<sub>3</sub> with AgEF<sub>n</sub>. The reactions were conducted in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (Scheme 1). In all cases, a white-gray solid appeared, suggesting an efficient chloride abstraction with precipitation of AgCl. Gas emission was observed with AgBF<sub>4</sub> and AgPF<sub>6</sub> (presumably BF<sub>3</sub> or PF<sub>5</sub>). <sup>19</sup>F nuclear magnetic resonance (NMR) spectra of the filtrates were recorded immediately, indicating the absence of

**Scheme 1.** Reaction of IPr-GaCl<sub>3</sub> with AgEF<sub>n</sub> (EF<sub>n</sub> = SbF<sub>6</sub>, PF<sub>6</sub>, or BF<sub>4</sub>)

the starting silver salts. Single fluorinated species arising from IPr-GaCl<sub>3</sub>/AgSbF<sub>6</sub> and IPr-GaCl<sub>3</sub>/AgBF<sub>4</sub> were found as singlets at −121.3 and −144.9 ppm, respectively. In the mixture resulting from IPr-GaCl<sub>3</sub>/AgPF<sub>6</sub>, at least three species were detected in the <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P spectra (see the Supporting Information). The major compound, which gave a doublet in the <sup>19</sup>F NMR spectrum (<sup>1</sup>J<sub>PF</sub> = 1066 Hz), vanished over time.

Colorless monocrystalline compounds were collected in cases in which AgSbF<sub>6</sub> and AgBF<sub>4</sub> had been used (**1a** and **1b**, respectively). These solids were subjected to X-ray diffraction analyses, which clearly indicated the substitution of one chlorine atom with the perfluoro anion (Figure 1).<sup>21</sup>



**Figure 1.** Crystal structures of **1a** (left) and **1b** (right) (thermal ellipsoids at the 30% probability level; hydrogen atoms omitted for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees) in complex **1a**: Ga–Cl(1), 2.128(2); Ga–Cl(2), 2.127(2); Ga–F(1), 1.920(4); Ga–C(1), 1.987(5); Sb–F(1), 1.987(4); Sb–F(2), 1.877(4); Sb–F(3), 1.879(5); Sb–F(4), 1.866(4); Sb–F(5), 1.855(4); Sb–F(6), 1.888(5); Ga–F(1)–Sb, 145.6(2). Selected bond lengths (angstroms) and angles (degrees) in complex **1b**: Ga–Cl(1), 2.120(2); Ga–Cl(2), 2.130(1); Ga–F(1), 1.877(2); Ga–C(1), 1.988(2); B–F(1), 1.539(4); B–F(2), 1.350(4); B–F(3), 1.357(4); B–F(4), 1.354(4); Ga–F(1)–B, 135.7(2).

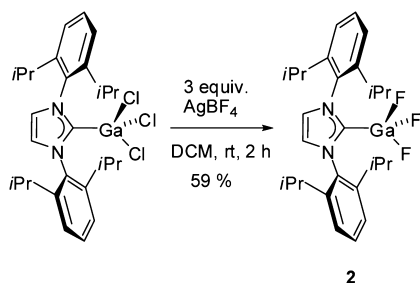
Of particular interest, complexes **1a** and **1b** showed catalytic activity for the reaction depicted in Table 1 similar to that of the corresponding IPr-GaCl<sub>3</sub>/AgEF<sub>n</sub> mixtures, i.e., excellent catalytic activity for **1a** and almost no conversion with **1b**.

These two complexes display a fluorine atom that bridges gallium and antimony or gallium and boron [F(1)]. In **1a**, the Sb–F(1) distance of 1.987(4) Å is significantly longer than the other five Sb–F bonds (1.86–1.88 Å). The Ga–F(1) distance of 1.920(4) Å is also longer than typical covalent Ga–F bonds (1.75–1.80 Å). Of particular interest, the angles between equatorial fluorine atoms F(2–5) and bridging fluorine atom F(1) are smaller than 90° [average of 86.8(2)°], which suggests an increase in the *s* character of antimony. Thus, the solid state structure can be viewed in its extremes either as [IPr-GaCl<sub>2</sub>][SbF<sub>6</sub>] or as [IPr-GaCl<sub>2</sub>F·SbF<sub>5</sub>]. In **1b**, the Ga–F(1) distance is even shorter than in **1a** [1.877(2) Å]. The B–F(1) bond [1.539(4) Å] is much longer than the nonbridged B–F bonds (1.35–1.36 Å). The sum of the F–B–F(1) angles of 314.7(6)° shows a strong deviation from tetrahedral geometry, also indicating an increase in *s* character. Actually, the boron atom is located only 0.35 Å above the plane defined by F(2), F(3), and F(4). Clearly, this structure seems to be best described as [IPr-GaCl<sub>2</sub>F·BF<sub>3</sub>]. The existence of fluorine-bridged species in solution can sometimes be ascertained by <sup>19</sup>F NMR.<sup>22</sup> At low temperatures, anion spinning can be slowed so much that the bridging fluoride becomes distinguishable.<sup>23</sup> At 210 K, the fluorine nuclei of the [SbF<sub>6</sub>]<sup>−</sup> adduct split in three: a sharp signal at −131.8 ppm, a broad signal at −118.7 ppm, and a doublet at −110.3 ppm (*J* = 102.4 Hz). Unfortunately, the

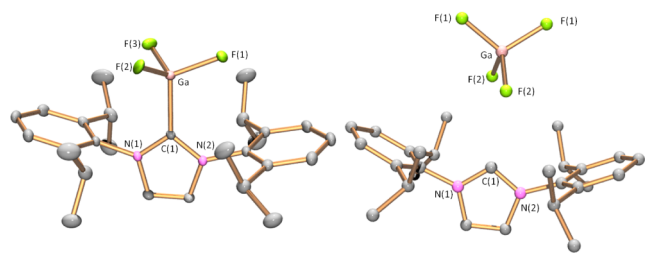
quadrupolar couplings to the two antimony and gallium isotopes prevented resolution. The same splitting of the  $^{19}\text{F}$  signals was observed with the  $[\text{BF}_4]^-$  adduct at 210 K, yet again resolution was not reached.

$[\text{SbF}_6]^-$ ,  $[\text{PF}_6]^-$ , and  $[\text{BF}_4]^-$  adducts in which the anion coordinates in a monodentate monocoordinate fashion<sup>24</sup> to transition metal cations are quite common.<sup>22,25</sup> On the other hand, only four of such species in which the anion is monocoordinated to a p-block metal have been described, all with  $[\text{BF}_4]^-$ .<sup>26</sup> According to their geometrical parameters, which show a weakly perturbed  $\text{BF}_4$  moiety, none of these complexes seem so close to eliminate  $\text{BF}_3$  as **1b**. In that respect, **1b** releases acidic fumes when exposed to air. The behavior of the adducts in the presence of a coordinating solvent (acetonitrile) was analyzed by ESI. For each of them, ion peaks corresponding to  $[\text{IPr}\cdot\text{GaCl}_m\text{F}_{3-m}]^+$  ( $m = 0, 1$ , or  $2$ ) could be detected. Because of the difficulty in separating these complexes,  $\text{IPr}\cdot\text{GaCl}_3$  was next treated with 3 equiv of  $\text{AgBF}_4$  (Scheme 2). Gas bubbles were clearly observed this time.

**Scheme 2.** Reactions of  $\text{IPr}\cdot\text{GaCl}_3$  with an Excess of  $\text{AgBF}_4$



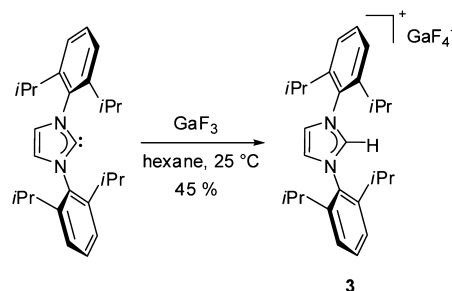
A new crystalline compound could be isolated in 59% yield. X-ray structure analysis revealed the complete replacement of the chloride ligands by fluorides (Figure 2, left).



**Figure 2.** Crystal structures of **2** (left) and **3** (right) (thermal ellipsoids at the 30% probability level; hydrogen atoms omitted for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees) in complex **2**: Ga–F(1), 1.774(1); Ga–F(2), 1.7689(8); Ga–F(3), 1.853(1); Ga–C(1), 1.991(1); C(1)–Ga–F(1), 112.34(5); C(1)–Ga–F(2), 110.87(4); C(1)–Ga–F(3), 111.32(5). Selected bond lengths (angstroms) and angles (degrees) in complex **3**: Ga–F(1), 1.757(1); Ga–F(2), 1.749(2).

It is worth noting that the direct reaction of  $\text{IPr}$  with  $\text{GaF}_3$  did not yield  $\text{IPr}\cdot\text{GaF}_3$  but the imidazolium salt  $[\text{IPrH}][\text{GaF}_4]$  (Scheme 3), as shown by X-ray structure analysis (Figure 2, right). The formation of such salts after the direct reaction of  $\text{MX}_3$  ( $M$  is a group 13 metal) with a NHC has already been observed and was explained by the presence of adventitious water giving rise to the imidazolium of  $\text{MX}_4^+$  and  $\text{MX}_2\text{OH}^-$  as side products.<sup>27</sup> Thus, the controlled decomposition of  $[\text{BF}_4]^-$

**Scheme 3.** Reactions of  $\text{IPr}$  with  $\text{GaF}_3$



to deliver  $\text{F}^{28}$  represents an expedient way to generate Ga–F bonds from Ga–Cl bonds under mild conditions.<sup>29</sup>

In agreement with the results shown in Table 1,  $\text{IPr}\cdot\text{GaF}_3$  proved to be catalytically impotent.

As our experimental observations suggest,  $[\text{IPr}\cdot\text{GaCl}_2]^+$  has a strong fluorine ion affinity (FIA),<sup>30</sup> actually higher than that of  $\text{BF}_3$ . This is consistent with the FIA of  $\text{GaCl}_3$  (432 kJ/mol) versus that of  $\text{BF}_3$  (338 kJ/mol).<sup>31</sup> On the other hand, the large FIA of  $\text{SbF}_5$  (489 kJ/mol) explains the stability of the  $[\text{SbF}_6]^-$  adduct in the absence of additional ligands. As for  $[\text{PF}_6]^-$ , the lower FIA of  $\text{PF}_5$  (394 kJ/mol) compared to that of  $\text{GaCl}_3$  supports a deactivation pathway of the catalyst similar to the  $[\text{BF}_4]^-$  case. Calculations at the BP86/Def2-SVPD//MP2/Def2-TZVPP level of theory were conducted on a model NHC–gallium complex to confirm this trend (Table 2). The exchange

**Table 2.** Computed Gibbs Free Energies of Fluoride Abstraction

entry	$[\text{EF}_n]^-$	L	$\Delta G_{\text{BP86}}$ (kcal/mol)	$\Delta G_{\text{MP2}}$ (kcal/mol)
1	$\text{SbF}_6^-$	none	−68.8	−70.2
2	$\text{PF}_6^-$	none	−88.5	−98.2
3	$\text{BF}_4^-$	none	−99.6	−104.9
4	$\text{SbF}_6^-$	$\text{Me}_2\text{O}$	3.0	4.6
5	$\text{PF}_6^-$	$\text{Me}_2\text{O}$	1.2	1.9
6	$\text{BF}_4^-$	$\text{Me}_2\text{O}$	−1.5	−0.02

of fluoride from  $[\text{EF}_n]^-$  to  $[\text{NHC}\cdot\text{GaCl}_2]^+$  becomes more exergonic as the expected stability of the perfluoro anion decreases:  $[\text{SbF}_6]^- > [\text{PF}_6]^- > [\text{BF}_4]^-$  (entries 1–3). Under catalytic conditions, a ligand could facilitate the release of  $\text{EF}_{n-1}$  from  $\text{NHC}\cdot\text{GaCl}_2(\mu\text{-F})\text{EF}_{n-1}$ .  $\text{Me}_2\text{O}$  was chosen in the calculations to model an oxygenated functionality of the organic substrates displayed in Table 1. As shown in entries 4–6, the free energies are quite low, even in the case of antimony.<sup>32</sup>

Thus, the formation of  $\text{SbF}_5$  under the catalytic conditions is conceivable. In fact, we noticed that the reaction depicted in Table 1 takes place in the presence of  $\text{SbF}_5$  (5 mol %; 12% conversion after 2 h; 70% conversion after 24 h). However, the rate of the transformation is much slower than with  $\text{IPr}\cdot\text{GaCl}_3/\text{AgSbF}_6$  [99% conversion after 2 h (see Table 1, entry 1)], which rules out the sole intervention of  $\text{SbF}_5$ .<sup>33</sup> Also, in agreement with the experimental results,  $\text{BF}_3\cdot\text{OEt}_2$ , which is a hard noncarbophilic Lewis acid, is not an active catalyst.<sup>34</sup> Thus, it is likely that  $\text{IPr}\cdot\text{GaCl}_2^+$  is the real catalyst and not the Lewis acid arising from the decomposition of the anion.



## CONCLUSION

We describe the synthesis of novel fluorine-bridged gallium complexes **1a** and **1b**, as well as gallium trifluoride **2**. These complexes were formed upon treatment of  $\text{IPr-GaCl}_3$  with silver salts exhibiting perfluoro anions. The formation of **2** explains the incapacity of the  $\text{IPr-GaCl}_3/\text{AgPF}_6$  and  $\text{IPr-GaCl}_3/\text{AgBF}_4$  systems to catalyze a cycloisomerization Friedel–Crafts tandem reaction that requires the presence of a soft  $\pi$ -Lewis acid. Although perfluoro anions are usually versatile in transition metal catalysis, the development of reactions catalyzed by cationic main group elements will be contingent upon the use of the most robust anions. In this case,  $\text{SbF}_6^-$  is stable enough, yet its cleavage by cationic silicon and germanium species has been described previously.<sup>14a</sup> Thus, we will now investigate other classes of anions, such as fluorinated alkoxyaluminate.<sup>1</sup>

## EXPERIMENTAL SECTION

**General Information.** All reactions were conducted using standard Schlenk techniques under a positive pressure of argon. Unless otherwise stated, commercially available reagents were used as received without further purification. Gallium(III) halides were obtained from Alfa Aesar. Dichloroethane, dichloromethane, and dichloromethane- $d_2$  were distilled from calcium hydride and degassed prior to being used by three consecutive freeze–pump–thaw cycles. NMR spectra were recorded on AM250, AV300, AV360, and DRX400 MHz Bruker spectrometers. Chemical shifts are given in parts per million. The spectra were calibrated to the residual  $^1\text{H}$  and  $^{13}\text{C}$  signals of the solvent. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad), coupling constants ( $J$ ), and integration. Because of the quadrupole moments of  $^{69}\text{Ga}/^{71}\text{Ga}$  nuclei, carbon atoms bound to gallium are not observed in  $^{13}\text{C}$  NMR.<sup>35</sup>  $^{71}\text{Ga}$  (122.0 MHz) NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ . Complexes **1a** and **1b** are not observed via  $^{71}\text{Ga}$  NMR because of their low symmetry.<sup>36</sup> Complex **2**, which has  $C_{3v}$  symmetry, should be observable. However, it is subject to rapid relaxation, and the signal is lost in the noise. This phenomenon is typical of complexes exhibiting Ga–F bonds.<sup>37</sup>  $[\text{GaX}_4]^-$  anions that have  $T_d$  symmetry usually give sharp peaks in  $^{71}\text{Ga}$  NMR.<sup>36</sup> For the reasons given above,<sup>37</sup> this is not the case when  $X = \text{F}$  (complex **3**) for which a broad peak was obtained nonetheless. HRMS was performed on a MicrOTOFq Bruker spectrometer. Reproducible microanalyses could not be obtained. X-ray diffraction data for **1a**, **1b**, **2**, and **3** were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as a cryoprotectant and then flash-frozen in a nitrogen gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device with accuracy of  $\pm 1 \text{ K}$ . The data were corrected for Lorentz polarization and absorption effects. The structures were determined by direct methods using SHELXS-97<sup>38</sup> and refined against  $F^2$  by full-matrix least-squares techniques using SHELXL-97<sup>39</sup> with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.<sup>40</sup> The crystal data collection and refinement parameters are listed in the Supporting Information. CCDC 965598–965601 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/Community/Requestastructure>.

**Compound 1a.** To a solution of  $\text{IPr-GaCl}_3^{35e}$  (41 mg, 72  $\mu\text{mol}$ ) in dichloromethane- $d_2$  (1 mL) was added  $\text{AgSbF}_6$  (25 mg, 72  $\mu\text{mol}$ ) in

one portion at room temperature in a glovebox. A precipitate formed instantly. The reaction mixture was stirred for 30 min, and the suspension was filtered off. The resulting clear solution was directly analyzed by NMR. Single crystals were grown in a 1/1  $\text{CH}_2\text{Cl}_2$ /hexane mixture. The colorless needles were collected and dried under vacuum (35 mg, 45  $\mu\text{mol}$ , 62% yield).  $^1\text{H}$  NMR (250 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.68 (t,  $^3J = 7.7 \text{ Hz}$ , 2 H,  $\text{H}_{\text{Ph}}$ ), 7.62 (s, 2 H,  $\text{NCH}=\text{CHN}$ ), 7.44 (d,  $^3J = 7.7 \text{ Hz}$ , 4 H,  $\text{H}_{\text{Ph}}$ ), 2.45 [sept,  $^3J = 6.8 \text{ Hz}$ , 4 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.36 (d,  $^3J = 6.8 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ), 1.20 (d,  $^3J = 6.8 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (232 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  –121.3.  $^{13}\text{C}$  NMR (62 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  147.6, 132.1, 128.2, 125.6, 124.6, 30.1, 26.3, 23.1. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{36}\text{Cl}_2\text{FGaNa}_2\text{Na}$  [ $\text{M} - \text{SbF}_5 + \text{Na}$ ] $^+$ , 569.1388; found, 569.1533.

**Compound 1b.** To a solution of  $\text{IPr-GaCl}_3^{35e}$  (58 mg, 102  $\mu\text{mol}$ ) in dichloromethane- $d_2$  (1 mL) was added  $\text{AgBF}_4$  (20 mg, 102  $\mu\text{mol}$ ) in one portion at room temperature in a glovebox. A precipitate formed instantly. The reaction mixture was stirred for 2 h, and the suspension was filtered off. The resulting clear solution was directly analyzed by NMR. The colorless solution was evaporated and dried under vacuum, yielding a solid (43 mg, 69  $\mu\text{mol}$ , 67% yield). Single crystals (needles) were grown in a 1/1  $\text{CH}_2\text{Cl}_2$ /hexane mixture.  $^1\text{H}$  NMR (250 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.66 (t,  $^3J = 7.8 \text{ Hz}$ , 2 H,  $\text{H}_{\text{Ph}}$ ), 7.55 (s, 2 H,  $\text{NCH}=\text{CHN}$ ), 7.44 (d,  $^3J = 7.8 \text{ Hz}$ , 4 H,  $\text{H}_{\text{Ph}}$ ), 2.47 [sept,  $^3J = 6.8 \text{ Hz}$ , 4 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.40 (d,  $^3J = 6.9 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ), 1.22 (d,  $^3J = 6.9 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (235 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  –144.9.  $^{13}\text{C}$  NMR (62 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  146.2, 132.9, 132.1, 128.2, 125.4, 29.9, 26.4, 22.8. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{36}\text{Cl}_2\text{GaNa}_2$  [ $\text{M} - \text{BF}_4$ ] $^+$ , 527.1506; found, 527.1498. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{36}\text{Cl}_2\text{FGaNa}_2\text{Na}$  [ $\text{M} - \text{BF}_3 + \text{Na}$ ] $^+$ , 569.1397; found, 569.1388.

**Compound 2.** To a solution of  $\text{IPr-GaCl}_3^{35e}$  (82 mg, 144  $\mu\text{mol}$ ) in dichloromethane- $d_2$  (1 mL) was added  $\text{AgBF}_4$  (84 mg, 434  $\mu\text{mol}$ ) in one portion at room temperature in a glovebox. A precipitate formed instantly. The mixture was stirred for 2 h, and the precipitate was filtered off. The clear solution was analyzed directly by NMR. The solvent was removed *in vacuo*. The resulting white residue was washed with hexane (2 mL) and dried *in vacuo* (44 mg, 85  $\mu\text{mol}$ , 59% yield). Single crystals were obtained by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution.  $^1\text{H}$  NMR (250 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.67 (t,  $^3J = 7.6 \text{ Hz}$ , 2 H,  $\text{H}_{\text{Ph}}$ ), 7.57 (s, 2 H,  $\text{NCH}=\text{CHN}$ ), 7.45 (d,  $^3J = 7.6 \text{ Hz}$ , 4 H,  $\text{H}_{\text{Ph}}$ ), 2.37 [sept,  $^3J = 6.6 \text{ Hz}$ , 4 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.32 (d,  $^3J = 6.9 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ), 1.18 (d,  $^3J = 6.9 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (235 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  –151.2.  $^{13}\text{C}$  NMR (62 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  146.3, 132.8, 131.9, 128.4, 125.4, 30.0, 26.2, 22.9. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{36}\text{F}_3\text{GaNa}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ , 537.1979; found, 527.1990.

**Compound 3.** To a solution of 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (87 mg, 0.25 mmol, 1 equiv) in hexane (10 mL) was added gallium(III) fluoride (38 mg, 0.3 mmol, 1.2 equiv) in one portion at room temperature. The reaction mixture was stirred overnight. The solvent was evaporated, and the residue was suspended in MeOH (10 mL). Complex **3** was isolated after filtration as a yellow foam (60 mg, 45% yield). Single crystals were grown from slow evaporation of  $\text{CDCl}_3$ .  $^1\text{H}$  NMR (250 MHz, 300 K,  $\text{CDCl}_3$ ):  $\delta$  8.73 (s, 1 H,  $\text{N}=\text{CH}-\text{N}$ ), 7.83 (s, 2 H,  $\text{NCH}=\text{CHN}$ ), 7.61 (t,  $^3J = 7.7 \text{ Hz}$ , 2 H,  $\text{H}_{\text{Ph}}$ ), 7.37 (d,  $^3J = 7.7 \text{ Hz}$ , 4 H,  $\text{H}_{\text{Ph}}$ ), 2.43 [sept,  $^3J = 6.8 \text{ Hz}$ , 4 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.30 (d,  $^3J = 6.8 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ), 1.22 (d,  $^3J = 6.8 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (235 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  –149.7.  $^{71}\text{Ga}$  NMR (122 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  145 (br s).  $^{13}\text{C}$  NMR (62 MHz, 300 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  147.3, 132.8, 131.0, 127.8, 124.6, 30.0, 25.8, 23.3. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{37}\text{N}_2\text{Na}$  [ $\text{M} - \text{GaF}_4 + \text{Na}$ ] $^+$ , 389.2956; found, 389.2970.

**General Procedure for the Bimolecular Dihydroarylation.**  $\text{AgX}$  (7 mol %) was added to a dichloroethane solution of the gallium(III) catalyst (5 mol %, 0.25 M) and the additive [10 mol % (Table 1, entries 4–11)] in a screw-cap vial under argon, and the mixture was stirred in the dark, at room temperature, for 5 min. Then, the arenynes (65 mg, 0.25 mmol, 1 equiv) and anisole (81  $\mu\text{L}$ , 3 equiv) were added, and the resulting mixture was stirred under the stated conditions and monitored by GC. Alternatively,  $\text{SbF}_5$  (5 mol %) or  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (5 mol %) was tested under the same conditions used for the Ga/Ag mixture. The reaction was quenched with  $\text{Et}_3\text{N}$  (1 drop)

and then the mixture diluted with diethyl ether (10 mL). The solution was filtered on a short pad of silica, which was rinsed with diethyl ether (5 mL). After evaporation, the crude was purified by flash chromatography (92:8 cyclohexane/EtOAc mixture).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

NMR spectra and energies of the computed species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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