ORGANOMETALLICS
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pubs.acs.org/Organometallics

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

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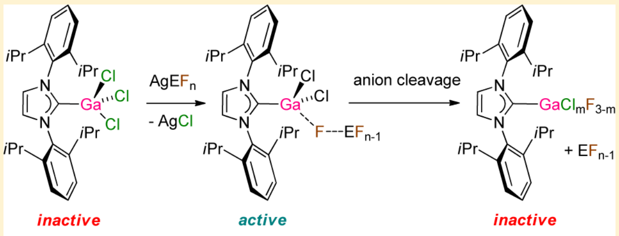
Supporting Information

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



(E = Sb, B; n = 6, 4; m = 0, 1, 2)

INTRODUCTION

It is now clearly established that weakly coordinating anions (WCAs)[1] are not always innocent bystanders in reactions catalyzed by cationic metal complexes.[2] 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.[3] This role of WCA in catalysis concerns not only chiral counterions but also simple and widely used anions such as SbF$_6^-$, PF$_6^-$, BF$_4^-$, etc.[4] Thus, knowing where the anion actually lies during the catalytic process is of prime importance.[5] 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 (tetraarylborates or perfluoro anions) by transition metal cations is a well-documented topic.[6−8] 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.[9]

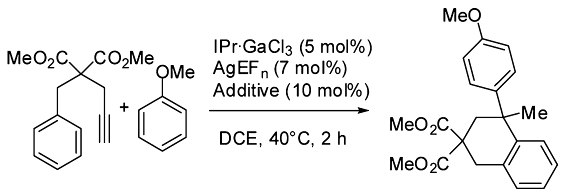
There is a clear trend in homogeneous catalysis to develop substitutes of the rarest late transition metals, notably through the use of abundant main group elements.[10] For instance, it was shown that neutral gallium salts can mimic the reactivity of iridium-, gold-, platinum-, or other noble metal-based catalysts in some reactions involving the activation of C−C π bonds.[11,12] 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.[13] Species such as [IPr·GaCl$_2$(L)][SbF$_6$] [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, and L = 2,4,6-trifluorobenzonitrile] were used as π-Lewis acids for the activation of alkynes toward nucleophilic attack. To study the influence of the anion on selectivity, we decided to use PF$_6^-$ and BF$_4^-$ instead of 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.[14] This study led us to characterize novel gallium F-bridged complexes of the type IPr·GaCl$_2$(μ-F)EF$_{n-1}$ (EF$_n$ = SbF$_6$ or BF$_4$) and gallium fluorides.

RESULTS AND DISCUSSION

We recently reported[13] that a mixture of IPr·GaCl$_3$[35e] and 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,[15] we then decided to study the influence of the silver salt. The use of AgPF$_6$ or AgBF$_4$ instead of AgSbF$_6$ resulted in a dramatic decrease in activity (entries 2 and 3).[16] Because neither IPr·GaCl$_3$ nor AgSbF$_6$ can by itself promote this transformation, it is likely that chloride abstraction takes place to generate [IPr·GaCl$_2$][SbF$_6$] as the active species. Thus, several hypotheses might explain the inactivity of the IPr·GaCl$_3$/AgPF$_6$ and IPr·GaCl$_3$/AgBF$_4$ systems. (i) The anion metathesis does not take place with AgPF$_6$ or AgBF$_4$. (ii) The substitution of the anion of [IPr·GaCl$_2$][EF$_n$] by the substrate does not take place when [EF$_n$]$^-$ = [PF$_6$]$^-$ or [BF$_4$]$^-$. (iii) [IPr·GaCl$_2$][EF$_n$] decomposes into inactive species when [EF$_n$]$^-$ = [PF$_6$]$^-$ or [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[17] in the reaction

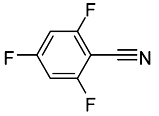
Received: December 16, 2013
Published: January 15, 2014

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



entry	AgEF$_n$	additive	GC conversion (%)
1	AgSbF$_6$	none	99
2	AgPF$_6$	none	2
3	AgBF$_4$	none	trace
4	AgSbF$_6$	L	97
5	AgPF$_6$	L	54
6	AgBF$_4$	L	1
7	AgSbF$_6$	[nBu$_4$N][SbF$_6$]	98
8	AgSbF$_6$	[nBu4N][PF$_6$]	47
9	AgSbF$_6$	[nBu$_4$N][BF$_4$]	5
10	AgPF$_6$	[nBu$_4$N][SbF$_6$]	97
11	AgBF$_4$	[nBu$_4$N][SbF$_6$]	73

L:

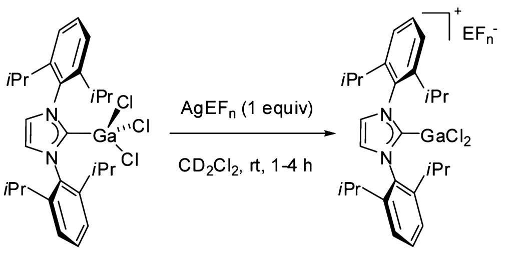


mixture, a significant improvement was observed with AgPF$_6$ (entry 5), but not with AgBF$_4$ (entry 6). Besides, the catalytic activity of the IPr·GaCl$_3$/AgSbF$_6$ mixture could be strongly diminished in the presence of [*n*Bu$_4$N][PF$_6$] (entry 8) and virtually shut down with [*n*Bu$_4$N][BF$_4$] (entry 9).[18,19] On the other hand, the IPr·GaCl$_3$/AgPF$_6$ and, to a lesser extent, IPr·GaCl$_3$/AgBF$_4$ systems became efficient when [*n*Bu$_4$N][SbF$_6$] was used as the additive (entries 10 and 11).[20] These control experiments suggest an efficient anion metathesis with each silver salt and rapid deactivation of [IPr·GaCl$_2$][PF$_6$] and especially [IPr·GaCl$_2$][BF$_4$]. 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$_3$ with AgEF$_n$. The reactions were conducted in CD$_2$Cl$_2$ 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$_4$ and AgPF$_6$ (presumably BF$_3$ or PF$_5$). ^{19}F nuclear magnetic resonance (NMR) spectra of the filtrates were recorded immediately, indicating the absence of the starting silver salts. Single fluorinated species arising from IPr·GaCl$_3$/AgSbF$_6$ and IPr·GaCl$_3$/AgBF$_4$ were found as singlets at −121.3 and −144.9 ppm, respectively. In the mixture resulting from IPr·GaCl$_3$/AgPF$_6$, at least three species were detected in the ^{1}H, ^{19}F, and ^{31}P spectra (see the Supporting Information). The major compound, which gave a doublet in the ^{19}F NMR spectrum ($^1J_{PF}$ = 1066 Hz), vanished over time.

Colorless monocrystalline compounds were collected in cases in which AgSbF$_6$ and AgBF$_4$ 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).[21]

Scheme 1. Reaction of IPr·GaCl$_3$ with AgEF$_n$ (EF$_n$ = SbF$_6$, PF$_6$, or BF$_4$)



1a (EF$_n$ = SbF$_6$, 62%)
1b (EF$_n$ = BF$_4$, 67%)
(EF$_n$ = PF$_6$, unstable material)

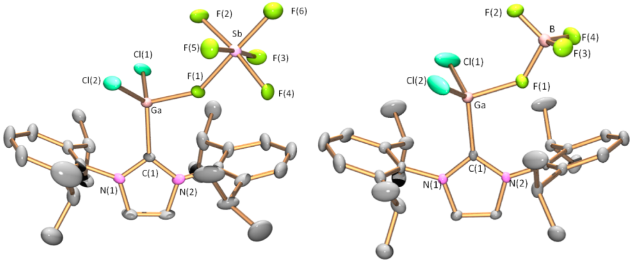


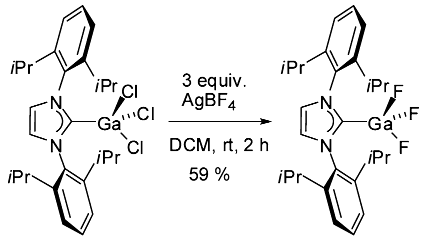
Figure 1. Crystal structures of **1a** (left) and **1b** (right) (thermal ellipsoids at the 30% probability level; hydrogen atoms omitted for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees) in complex **1a**: Ga−Cl(1), 2.128(2); Ga−Cl(2), 2.127(2); Ga−F(1), 1.920(4); Ga−C(1), 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$_3$/AgEF$_n$ 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$_2$][SbF$_6$] or as [IPr·GaCl$_2$F·SbF$_5$]. 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$_2$F·BF$_3$]. The existence of fluorine-bridged species in solution can sometimes be ascertained by ^{19}F NMR.[22] At low temperatures, anion spinning can be slowed so much that the bridging fluoride becomes distinguishable.[23] At 210 K, the fluorine nuclei of the [SbF$_6$]$^-$ 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}F signals was observed with the $[BF_4]^-$ adduct at 210 K, yet again resolution was not reached.

$[SbF_6]^-$, $[PF_6]^-$, and $[BF_4]^-$ adducts in which the anion coordinates in a monodentate monoconnective fashion[24] to transition metal cations are quite common.[22,25] 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 $[BF_4]^-$.[26] According to their geometrical parameters, which show a weakly perturbed BF_4 moiety, none of these complexes seem so close to eliminate 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 $[IPr{\cdot}GaCl_mF_{3-m}]$ (m = 0, 1, or 2) could be detected. Because of the difficulty in separating these complexes, $IPr{\cdot}GaCl_3$ was next treated with 3 equiv of $AgBF_4$ (Scheme 2). Gas bubbles were clearly observed this time.

Scheme 2. Reactions of $IPr{\cdot}GaCl_3$ with an Excess of $AgBF_4$



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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).

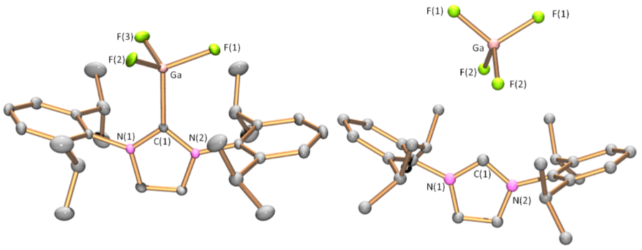
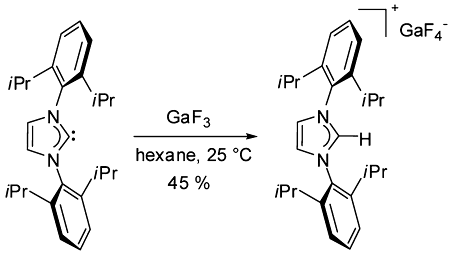


Figure 2. Crystal structures of **2** (left) and **3** (right) (thermal ellipsoids at the 30% probability level; hydrogen atoms omitted for the sake of clarity). Selected bond lengths (angstroms) and angles (degrees) in complex **2**: Ga−F(1), 1.774(1); Ga−F(2), 1.7689(8); Ga−F(3), 1.853(1); Ga−C(1), 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 IPr with GaF_3 did not yield $IPr{\cdot}GaF_3$ but the imidazolium salt $[IPrH][GaF_4]$ (Scheme 3), as shown by X-ray structure analysis (Figure 2, right). The formation of such salts after the direct reaction of 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 MX_4^- and MX_2OH as side products.[27] Thus, the controlled decomposition of $[BF_4]^-$ to deliver F^-[28] represents an expedient way to generate Ga−F bonds from Ga−Cl bonds under mild conditions.[29]

Scheme 3. Reactions of IPr with GaF_3

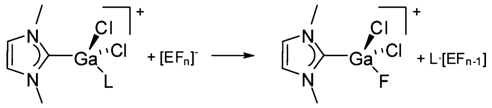


3

In agreement with the results shown in Table 1, $IPr{\cdot}GaF_3$ proved to be catalytically impotent.

As our experimental observations suggest, $[IPr{\cdot}GaCl_2]^+$ has a strong fluorine ion affinity (FIA),[30] actually higher than that of BF_3. This is consistent with the FIA of $GaCl_3$ (432 kJ/mol) versus that of BF_3 (338 kJ/mol).[31] On the other hand, the large FIA of SbF_5 (489 kJ/mol) explains the stability of the $[SbF_6]^-$ adduct in the absence of additional ligands. As for $[PF_6]^-$, the lower FIA of PF_5 (394 kJ/mol) compared to that of $GaCl_3$ supports a deactivation pathway of the catalyst similar to the $[BF_4]^-$ 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 of fluoride from $[EF_n]^-$ to $[NHC{\cdot}GaCl_2]^+$ becomes more exergonic as the expected stability of the perfluoro anion decreases: $[SbF_6]^- > [PF_6]^- > [BF_4]^-$ (entries 1−3). Under catalytic conditions, a ligand could facilitate the release of EF_{n-1} from $NHC{\cdot}GaCl_2(\mu\text{-}F)EF_{n-1}$. Me_2O 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.[32]

Table 2. Computed Gibbs Free Energies of Fluoride Abstraction



entry	$[EF_n]^-$	L	ΔG_{BP86} (kcal/mol)	ΔG_{MP2} (kcal/mol)
1	SbF_6^-	none	−68.8	−70.2
2	PF_6^-	none	−88.5	−98 2
3	BF_4^-	none	−99.6	−104.9
4	SbF_6^-	Me_2O	3.0	4.6
5	PF_6^-	Me_2O	1.2	1.9
6	BF_4^-	Me_2O	−1.5	−0.02

Thus, the formation of 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 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 $IPr{\cdot}GaCl_3/AgSbF_6$ [99% conversion after 2 h (see Table 1, entry 1)], which rules out the sole intervention of SbF_5.[33] Also, in agreement with the experimental results, $BF_3{\cdot}OEt_2$, which is a hard noncarbophilic Lewis acid, is not an active catalyst.[34] Thus, it is likely that $IPr{\cdot}GaCl_2^+$ 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 IPr·$GaCl_3$ with silver salts exhibiting perfluoro anions. The formation of **2** explains the incapacity of the IPr·$GaCl_3$/$AgPF_6$ and IPr·$GaCl_3$/$AgBF_4$ systems to catalyze a cycloisomerization Friedel−Crafts tandem reaction that requires the presence of a soft π-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, SbF_6^- is stable enough, yet its cleavage by cationic silicon and germanium species has been described previously.[14a] Thus, we will now investigate other classes of anions, such as fluorinated alkoxyaluminates.[1]

■ 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}H and ^{13}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}Ga/^{71}Ga nuclei, carbon atoms bound to gallium are not observed in ^{13}C NMR.[35] ^{71}Ga (122.0 MHz) NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to $[Ga(H_2O)_6]^{3+}$. Complexes **1a** and **1b** are not observed via ^{71}Ga NMR because of their low symmetry.[36] 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.[37] $[GaX_4]^-$ anions that have T_d symmetry usually give sharp peaks in ^{71}Ga NMR.[36] For the reasons given above,[37] this is not the case when X = 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 Mo_K radiation (λ = 0.71073 Å). 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 ±1 K. The data were corrected for Lorentz polarization and absorption effects. The structures were determined by direct methods using SHELXS-97[38]and refined against F^2 by full-matrix least-squares techniques using SHELXL-9[39] 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.[40] 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 IPr·$GaCl_3$[35e] (41 mg, 72 μmol) in dichloromethane-d_2 (1 mL) was added $AgSbF_6$ (25 mg, 72 μmol) 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 CH_2Cl_2/hexane mixture. The colorless needles were collected and dried under vacuum (35 mg, 45 μmol, 62% yield). ^{1}H NMR (250 MHz, 300 K, CD_2Cl_2): δ 7.68 (t, ^3J = 7.7 Hz, 2 H, H_{Ph}), 7.62 (s, 2 H, NCH═CHN), 7.44 (d, ^3J = 7.7 Hz, 4 H, H_{Ph}), 2.45 [sept, ^3J = 6.8 Hz, 4 H, $C\underline{H}(CH_3)_2$], 1.36 (d, ^3J = 6.8 Hz, 12 H, CH_3), 1.20 (d, ^3J = 6.8 Hz, 12 H, CH_3). ^{19}F NMR (232 MHz, 300 K, CD_2Cl_2): δ −121.3. ^{13}C NMR (62 MHz, 300 K, CD_2Cl_2): δ 147.6, 132.1, 128.2, 125.6, 124.6, 30.1, 26.3, 23.1. HRMS (ESI) m/z: calcd for $C_{27}H_{36}Cl_2FGaN_2Na$ $[M - SbF_5 + Na]^+$, 569.1388; found, 569.1533.

Compound 1b. To a solution of IPr·$GaCl_3$[35e] (58 mg, 102 μmol) in dichloromethane-d_2 (1 mL) was added $AgBF_4$ (20 mg, 102 μmol) 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 μmol, 67% yield). Single crystals (needles) were grown in a 1/1 CH_2Cl_2/hexane mixture. ^{1}H NMR (250 MHz, 300 K, CD_2Cl_2): δ 7.66 (t, ^3J = 7.8 Hz, 2 H, H_{Ph}), 7.55 (s, 2 H, NCH═CHN), 7.44 (d, ^3J = 7.8 Hz, 4 H, H_{Ph}), 2.47 [sept, ^3J = 6.8 Hz, 4 H, $C\underline{H}(CH_3)_2$], 1.40 (d, ^3J = 6.9 Hz, 12 H, CH_3), 1.22 (d, ^3J = 6.9 Hz, 12 H, CH_3). ^{19}F NMR (235 MHz, 300 K, CD_2Cl_2): δ −144.9. ^{13}C NMR (62 MHz, 300 K, CD_2Cl_2): δ 146.2, 132.9, 132.1, 128.2, 125.4, 29.9, 26.4, 22.8. HRMS (ESI) m/z: calcd for $C_{27}H_{36}Cl_2GaN_2$ $[M - BF_4]^+$, 527.1506; found, 527.1498. HRMS (ESI) m/z: calcd for $C_{27}H_{36}Cl_2FGaN_2Na$ $[M - BF_3 + Na]^+$, 569.1397; found, 569.1388.

Compound 2. To a solution of IPr·$GaCl_3$[35e] (82 mg, 144 μmol) in dichloromethane-d_2 (1 mL) was added $AgBF_4$ (84 mg, 434 μmol) 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 μmol, 59% yield). Single crystals were obtained by slow evaporation of a CH_2Cl_2 solution. ^{1}H NMR (250 MHz, 300 K, CD_2Cl_2): δ 7.67 (t, ^3J = 7.6 Hz, 2 H, H_{Ph}), 7.57 (s, 2 H, NCH═CHN), 7.45 (d, ^3J = 7.6 Hz, 4 H, H_{Ph}), 2.37 [sept, ^3J = 6.6 Hz, 4 H, $C\underline{H}(CH_3)_2$], 1.32 (d, ^3J = 6.9 Hz, 12 H, CH_3), 1.18 (d, ^3J = 6.9 Hz, 12 H, CH_3). ^{19}F NMR (235 MHz, 300 K, CD_2Cl_2): δ −151.2. ^{13}C NMR (62 MHz, 300 K, CD_2Cl_2): δ 146.3, 132.8, 131.9, 128.4, 125.4, 30.0, 26.2, 22.9. HRMS (ESI) m/z: calcd for $C_{27}H_{36}F_3GaN_2Na$ $[M + Na]^+$, 537.1979; found, 527.1990.

Compound 3. To a solution of 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-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 $CDCl_3$. ^{1}H NMR (250 MHz, 300 K, $CDCl_3$): δ 8.73 (s, 1 H, N═CH−N), 7.83 (s, 2 H, NCH═CHN), 7.61 (t, ^3J = 7.7 Hz, 2 H, H_{Ph}), 7.37 (d, ^3J = 7.7 Hz, 4 H, H_{Ph}), 2.43 [sept, ^3J = 6.8 Hz, 4 H, $C\underline{H}(CH_3)_2$], 1.30 (d, ^3J = 6.8 Hz, 12 H, CH_3), 1.22 (d, ^3J = 6.8 Hz, 12 H, CH_3). ^{19}F NMR (235 MHz, 300 K, CD_2Cl_2): δ −149.7. ^{71}Ga NMR (122 MHz, 300 K, CD_2Cl_2): δ 145 (br s). ^{13}C NMR (62 MHz, 300 K, CD_2Cl_2): δ 147.3, 132.8, 131.0, 127.8, 124.6, 30.0, 25.8, 23.3. HRMS (ESI) m/z: calcd for $C_{27}H_{37}N_2Na$ $[M - GaF_4 + Na]^+$, 389.2956; found, 389.2970.

General Procedure for the Bimolecular Dihydroarylation. 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 arenyne (65 mg, 0.25 mmol, 1 equiv) and anisole (81 μL, 3 equiv) were added, and the resulting mixture was stirred under the stated conditions and monitored by GC. Alternatively, SbF_5 (5 mol %) or BF_3·Et_2O (5 mol %) was tested under the same conditions used for the Ga/Ag mixture. The reaction was quenched with Et_3N (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.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from Université Paris-Sud, MESR, CNRS, and IUF. We also thank Dr. Marie Sircoglou and Jean-Pierre Baltaze for useful discussions. We used the computing facility of the CRIHAN (Project 2006-013).

■ REFERENCES

(1) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(2) Macchioni, A. *Chem. Rev.* **2005**, *105*, 2039.

(3) For recent reviews, see: (a) Lacour, J.; Moraleda, D. *Chem. Commun.* **2009**, 7073. (b) Phipps, R. J.; Hamilton, G. L.; Toste, F. D. *Nat. Chem.* **2012**, *4*, 603. (c) Mahlau, M.; List, B. *Isr. J. Chem.* **2012**, *52*, 630. (d) Ávila, E. P.; Amarante, G. W. *ChemCatChem* **2012**, *4*, 1713. (e) Parra, A.; Reboredo, S.; Martín Castro, A. M.; Alemán. *J. Org. Biomol. Chem.* **2012**, *10*, 5001. (f) Brak, K.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2013**, *52*, 534. (g) Mahlau, M.; List, B. *Angew. Chem., Int. Ed.* **2013**, *52*, 518.

(4) For remarkable perfluoro anion effects in stereoselective catalysis, see: (a) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 798. (b) Bonaccorsi, C.; Mezzetti, A. *Organometallics* **2005**, *24*, 4953.

(5) See, for instance: (a) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Terenzi, S. *Organometallics* **1996**, *15*, 4349. (b) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1219. (c) Macchioni, A. *Eur. J. Inorg. Chem.* **2003**, 195. (d) Zuccaccia, D.; Belpassi, L.; Tarantelli, F.; Macchioni, A. *J. Am. Chem. Soc.* **2009**, *131*, 3170. (e) Barbazanges, M.; Augé, M.; Moussa, J.; Amouri, H.; Aubert, C.; Desmarets, C.; Fensterbank, L.; Gandon, V.; Malacria, M.; Ollivier, C. *Chem.—Eur. J.* **2011**, *17*, 13789. (f) Arthuis, M.; Beaud, R.; Gandon, V.; Roulland, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 10510. (g) Ciancaleoni, G.; Biasiolo, L.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D.; Belpassi, L. *Organometallics* **2013**, *32*, 4444.

(6) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(7) For examples of cleavage of perfluoro anions in the transition metal series, see: (a) Reedijk, J.; Jansen, J. C.; van Koningsveld, H.; van Kralingen, C. G. *Inorg. Chem.* **1978**, *17*, 1990. (b) Ten Hoedt, R. W. M.; Reedijk, J. *Inorg. Chim. Acta* **1981**, *51*, 23. (c) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452. (d) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808. (e) de Frémont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* **2009**, *694*, 551.

(8) For examples of cleavage of tetraaryl borates in the transition metal series, see: (a) Salem, H.; Shimon, L. J. W.; Leitus, G.; Weiner, L.; Milstein, D. *Organometallics* **2008**, *27*, 2293. (b) Weber, S. D.; Zahner, D.; Rominger, F.; Straub, B. F. *Chem. Commun.* **2012**, *48*, 11325.

(9) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

(10) Power, P. P. *Nature* **2010**, *463*, 171.

(11) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268.

(12) For examples of the use of Ga(III) halides as π-Lewis acids, see: (a) Inoue, H.; Chatani, N.; Murai, S. *J. Org. Chem.* **2002**, *67*, 1414. (b) Chatani, N.; Inoue, H.; Kotsuma, T.; Murai, S. *J. Am. Chem. Soc.* **2002**, *124*, 10294. (c) Peppers, B. P.; Diver, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 9524. (d) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (e) Lee, S. I.; Sim, S. H.; Kim, S. M.; Kim, K.; Chung, Y. K. *J. Org. Chem.* **2006**, *71*, 7120. (f) Kim, S. M.; Lee, S. I.; Chung, Y. K. *Org. Lett.* **2006**, *8*, 5425. (g) Simmons, E. M.; Sarpong, R. *Org. Lett.* **2006**, *8*, 2883. (h) Li, H.-J.; Guillot, R.; Gandon, V. *J. Org. Chem.* **2010**, *75*, 8435. (i) de Jesus Cortez, F.; Sarpong, R. *Org. Lett.* **2010**, *12*, 1428. (j) Yadav, J. S.; Reddy, B. V. S.; Padmavani, B.; Gupta, M. K. *Tetrahedron Lett.* **2004**, *45*, 7577. (k) Yadav, J. S.; Reddy, B. V. S.; Biswas, S. K.; Sengupta, S. *Tetrahedron Lett.* **2009**, *50*, 5798. (l) Pascual, S.; Bour, C.; de Mendoza, P.; Echavarren, A. M. *Beilstein J. Org. Chem.* **2011**, *7*, 1520.

(13) Tang, S.; Monot, J.; El-Hellani, A.; Michelet, B.; Guillot, R.; Bour, C.; Gandon, V. *Chem.—Eur. J.* **2012**, *18*, 10239.

(14) (a) Marks, T. J. *Inorg. Chem.* **1974**, *13*, 1624. (b) Farooq, O. *J. Fluorine Chem.* **1997**, *86*, 189. (c) Farooq, O. *J. Chem. Soc., Perkin Trans. 1* **1998**, 661. (d) Jorapur, Y. R.; Shimada, T. *Synlett* **2012**, 1064. (e) Farina, P.; Latter, T.; Levason, W.; Reid, G. *Dalton Trans.* **2013**, *42*, 4714.

(15) (a) El-Hellani, A.; Monot, J.; Guillot, R.; Bour, C.; Gandon, V. *Inorg. Chem.* **2013**, *52*, 506. (b) El-Hellani, A.; Monot, J.; Tang, S.; Guillot, R.; Bour, C.; Gandon, V. *Inorg. Chem.* **2013**, *52*, 11493.

(16) Likewise, in the $GaCl_3/AgEF_n$-catalyzed Friedel−Crafts acylation, the reaction proceeds with $AgSbF_6$ but not with $AgPF_6$ or $AgBF_4$: Mukaiyama, T.; Ohno, T.; Nishimura, T.; Suda, S.; Kobayashi, S. *Chem. Lett.* **1991**, 1059.

(17) The choice of this nitrile comes from our earlier study (see ref 13).

(18) In these experiments, the ammonium salt was mixed with IPr·$GaCl_3$ before the silver salt was introduced. If the silver salt is added first, the conversions are 72 and 7%, respectively.

(19) IPr·$GaCl_3/[nBu_4N][EF_n]$ mixtures are catalytically impotent.

(20) Conversions of 36 and 15%, respectively, were recorded when the ammonium salt was added after the silver salt.

(21) There are actually two isomers of **1b** in the unit cell that differ by the orientation of the BF_3 moiety. Only one isomer is discussed, yet the same conclusions are reached with the other.

(22) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869.

(23) Herrmann, W. A.; Zybill, C. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)*; Herrmann, W. A., Salzer, A., Eds.; Thieme: Stuttgart, Germany, 1996; Vol. *8*.

(24) Roesky, H. W.; Haiduc, I. *Dalton Trans.* **1999**, 2249.

(25) (a) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (b) Bröchler, R.; Sham, I. H. T.; Bodenbinder, M.; Schmitz, V.; Rettig, S. J.; Trotter, J.; Willner, H.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 2172. (c) LeBlond, N.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 2473. (d) Khorasani-Motlagh, M.; Safari, N.; Noroozifar, M.; Shahroosvand, H.; Parsaii, Z.; Patrick, B. O. *Inorg. Chim. Acta* **2007**, *360*, 2331. (e) Elliott, H. S. A.; Lehmann, J. F.; Mercier, H. P. A.; Jenkins, H. D. B.; Schrobilgen, G. J. *Inorg. Chem.* **2010**, *49*, 8504. (f) Dub, P. A.; Belkova, N. V.; Filippov, J.-O. A.; Daran, C.; Epstein, L. M.; Lledós, A.; Shubina, E. S.; Poli, R. *Chem.—Eur. J.* **2010**, *16*, 189.

(26) For Sn: (a) Grützmacher, H.; Pritzkow, H. *Organometallics* **1991**, *10*, 938. (b) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295. For Bi: (c) Zhang, X.; Qiu, R.; Tan, N.; Yin, S.; Xia, J.; Luo, S.; Au, C.-T. *Tetrahedron Lett.* **2010**, *51*, 153.

(27) (a) Baker, R. J.; Davies, A. J.; Jones, C.; Kloth, M. *J. Organomet. Chem.* **2002**, *656*, 203. (b) Stasch, A.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2004**, 4052.

(28) Reger, D. L.; Watson, R. P.; Gardinier, J. R.; Smith, M. D.; Pellechia, P. J. *Inorg. Chem.* **2006**, *45*, 10088.

(29) For the use of CsF, see: Kopp, M. R.; Kräuter, T.; Werner, B.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1998**, *624*, 881.

(30) (a) Mallouk, T. E.; Rosenthal, G. R.; Müller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167. (b) Jenkins, H.; Krossing, I.; Passmore, J.; Raabe, I. *J. Fluorine Chem.* **2004**, *125*, 1585. (c) Krossing, I.; Raabe, I. *Chem.—Eur. J.* **2004**, *10*, 5017.

(31) Müller, L. O.; Himmel, D.; Stauffer, J.; Steinfeld, G.; Slattery, J.; Santiso-Quiñones, G.; Brecht, V.; Krossing, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 7659.

(32) On the arenyne displayed in Table 1, the oxygen atoms of the esters are better ligands than the reacting alkyne moiety. For instance, when L = acetylene and $[EF_n]^-$ = SbF_6^-, the MP2 free energy is 20.4 kcal/mol instead of 3.0 kcal/mol when L = Me_2O.

(33) The complex $[IPr\cdot GaCl_2(2,4,6\text{-}F_3\text{-}C_6H_2\text{-}CN)][SbF_6]$ is also more efficient than SbF_5 (see ref 13).

(34) PF_5 is not readily available.

(35) This is also the case for the majority of NHC adducts to group 13 metals. See *inter alia*: (a) Li, X.-W.; Su, J.; Robinson, G. H. *Chem. Commun.* **1996**, 2683. (b) Black, S. J.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Abdul Malik, K. M.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **1997**, 4313. (c) Abernethy, C. D.; Cole, M. L.; Jones, C. *Organometallics* **2000**, *19*, 4852. (d) Cole, M. L.; Davies, A. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2451. (e) Marion, N.; Escudo-Adán, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Organometallics* **2007**, *26*, 3256. (f) Cole, M. L.; Furfari, S. K.; Kloth, M. *J. Organomet. Chem.* **2009**, *694*, 2934. (g) Bantu, B.; Pawar, G. M.; Wurst, K.; Decker, U.; Schmidt, A. M.; Buchmeiser, M. R. *Eur. J. Inorg. Chem.* **2009**, 1970. (h) Muthaiah, S.; Do, D. C. H.; Ganguly, R.; Vidović, D. *Organometallics* **2013**, *32*, 6718.

(36) Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2007**, *46*, 7215.

(37) Buslaev, Y. A.; Petrosyants, S. P.; Tarasov, V. P. *J. Struct. Chem.* **1974**, *15*, 187.

(38) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(39) Sheldrick, G. M. *SHELXL-97, Program for the refinement of crystal structures from diffraction data*; University of Göttingen: Göttingen, Germany, 1997.

(40) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.