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# Cationic Gallium(III) Halide Complexes: a New Generation of $\pi$ -Lewis Acids

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Gallium(III) halides are powerful Lewis acids that are used in a variety of catalytic transformations. These salts are strong oxo-, thio- or azaphilic  $\sigma$ -Lewis acids, yet they are also able to activate simple olefins and alkynes [Eq. 1].<sup>[1,2]</sup> For instance, as  $\sigma$ -Lewis acids, they catalyze nucleophilic additions to epoxides,<sup>[3]</sup> 1,4-addition to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds,<sup>[4]</sup> Nazarov reactions,<sup>[5]</sup> skeletal rearrangement of aldehydes,<sup>[6]</sup> allylation of imines,<sup>[7]</sup> sulfidation of alkynes or alkenes,<sup>[8]</sup> as well as C–C bond formation involving C–H,<sup>[9]</sup> N–H,<sup>[10]</sup> and O–H<sup>[11]</sup> bond activation. As  $\pi$ -Lewis acids, GaX<sub>3</sub> salts catalyze inter- and intramolecular nucleophilic additions to alkynes and alkenes.<sup>[12]</sup>

$$X_3Ga$$
  
 $Nu^-$   
 $Harrow$   
 $Sat}$   
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 $Nu^-$   
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 $Nu^-$ 

In spite of their capabilities, gallium(III) halides are not widely used and keep giving rise to mistrust from the synthetic chemists' community. The main reasons are: 1) the difficulty in handling these species due to their highly hygroscopic nature, and 2) the presupposed ill-defined nature of the intermediates, which makes the anticipation and the rationalization of the results quite difficult.<sup>[13]</sup> The issue of hygroscopy is indeed a critical one; even after taking precautions, hydration products can be observed, sometimes in large amounts.<sup>[12h]</sup>  $Ga(OH)Cl_2$ , which would arise from adventitious hydrolysis, has even been proposed as the active species of a coupling reaction catalyzed by GaCl<sub>3</sub>.<sup>[14]</sup> Thus, high loadings are usually required, typically between 10 and 100 mol%, to ensure a sufficient concentration of intact catalyst. In this context, the use of well-defined air- and moisture-stable L·GaX<sub>3</sub> adducts seems highly desirable to ensure further development of Ga<sup>III</sup>-catalyzed transformations.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201202.

Among these, a few examples of N-heterocyclic carbene– $GaX_3$  adducts have been reported.<sup>[15]</sup> However, the stabilization of  $GaX_3$  by a strongly coordinating ligand will certainly be detrimental to its reactivity. To generate an active species, one could think of opening a vacant site on gallium by halide abstraction, that is, by using a silver salt [Eq. 2].

$$L^{1}-\underset{\mathbf{x}}{\overset{X}{\xrightarrow{}}} \xrightarrow{Ag^{+}, L^{2}} L^{1}-\underset{\mathbf{x}}{\overset{L^{2}}{\xrightarrow{}}} L^{1}-\underset{\mathbf{x}}{\overset{L^{2}}{\xrightarrow{}}}$$
(2)

Yet such additives are also, to some extent, moisture- and light-sensitive, and can interfere with the catalytic process. The use of isolated complexes of type  $L^1L^2GaX_2^+$ , in which  $L^1$  is a strongly coordinating ligand and  $L^2$  is a weakly coordinating ligand (ergo exchangeable by the substrate), could prevent the systematic use of a silver salt. To the best of our knowledge, there are no applications of such well-defined complexes in catalysis. They would be particularly interesting in the field of  $\pi$ -catalysis, in which expensive noble metal complexes (Au, Pt, Ir, Rh, and so on) are mostly used.<sup>[16,17]</sup>

Several (NHC)GaX<sub>3</sub> adducts (**1a–f**, X=Cl, Br, I) were prepared by the free carbene method<sup>[15b,c,18]</sup> and proved indeed much easier to handle than GaX<sub>3</sub> salts (Scheme 1).

In the absence of an additional ligand, we could not isolate the reaction product of  $(IPr)GaCl_3$  with  $AgSbF_6$ . Instead, we obtained a trace amount of the gallium(III) dihydroxide **3**, presumably resulting from the reaction of the expected unsaturated cationic gallium(III) dichloride with



Scheme 1. Neutral and cationic gallium(III) tri- and dihalides.

Chem. Eur. J. 2012, 00, 0-0

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adventitious water. The unusual structure of **3** could be established by single crystal X-ray structure analysis (see the Supporting Information).<sup>[19]</sup>

The desired cationic gallium(III) dichlorides  $2\mathbf{a}-\mathbf{d}$  were obtained by reproducing the above reaction in the presence of electron-rich and -poor benzonitrile derivatives (Scheme 1).<sup>[20,21,22]</sup> They were isolated in nearly quantitative yields after simple filtration of AgCl as kinetically stable yet quite moisture sensitive solids. Two of them,  $2\mathbf{a}$  and  $2\mathbf{c}$ , were crystallographically characterized (see Figure 1 and



Figure 1. ORTEP diagram of 2c with thermal ellipsoid at 50% probability level (hydrogens and  $\text{SbF}_6^-$  omitted for clarity).

Supporting Information).<sup>[19]</sup> The main feature of these tetrahedral gallium species is the N–Ga bond distance of 1.95 Å with 2,4,6-trimethoxybenzonitrile versus 1.99 Å with 2,4,6-triflurobenzonitrile, reflecting the weakest strength of interaction of the electron-poor derivative.

To test these neutral (1a-f) and cationic gallium complexes (2a-d), we carried out a one-pot cycloisomerization/ Friedel–Crafts tandem that we recently reported.<sup>[12h]</sup> This reaction involves consecutive triple C–C bond activation (cycloisomerization step) and a double C–C bond activation (Friedel–Crafts-type step). Although it stops at the cyclization step of the starting arenyne with neutral and cationic complexes of Au<sup>I</sup>, Pt<sup>IV</sup>, Ru<sup>II</sup>, and In<sup>III</sup>, it is catalyzed all the way by GaCl<sub>3</sub> or GaBr<sub>3</sub>, provided at least 10 mol% of these salts and a thoroughly dried solvent are used to avoid excessive catalyst decomposition and/or triple bond hydration of the starting arenyne.<sup>[23]</sup> Typically, this transformation requires 10 h in refluxing DCE to reach completion.



For instance, the reaction of arenyne **4** with anisole gives rise to product **5** in 88% yield with GaCl<sub>3</sub> as catalyst (Table 1, entry 1).<sup>[12b]</sup> As expected, (IPr)GaCl<sub>3</sub> was found totally unreactive (Table 1, entry 2). On the other hand, the adjunction of 5 mol% AgSbF<sub>6</sub> to 5 mol% of (IPr)GaCl<sub>3</sub> allowed the formation of **5** in 92% yield (Table 1, entry 3).<sup>[24]</sup> This result represents a significant improvement compared Table 1. Bimolecular reaction catalyzed by cationic gallium(III) dihalides generated in situ.

	E 4 (E = CO <sub>2</sub> Me)	OMe	L-GaX <sub>3</sub> (a mo AgSbF <sub>6</sub> (b mo DCE, 40 °C	1%) 1%) Me E E 5		.OMe
Entry	L	Х	a [mol %]	b [mol %]	<i>t</i> [h]	Yield [%] <sup>[a]</sup>
1	-	Cl	10	0	10	88 <sup>[b]</sup>
2	IPr ( <b>1</b> a)	Cl	5	0	48	0 <sup>[c]</sup>
3	IPr (1a)	Cl	5	5	2	92 (38) <sup>[d]</sup>
4	IPr (1a)	Cl	5	10	2	99 (68) <sup>[d]</sup>
5	IPr (1a)	Cl	5	15	2	99 (92) <sup>[d]</sup>
6	IPr (1a)	Cl	1	1	20	63
7	IPr (1a)	Cl	1	2	20	93
8	IPr (1a)	Cl	1	3	20	96
9	IPr (1a)	Cl	5	7	2	99
10	IPr (1b)	Br	5	7	2	99
11	IPr (1c)	Ι	5	7	2	95
12	SIPr (1d)	Cl	5	7	2	70
13	IMes (1e)	Cl	5	7	2	80
14	SIMes (1 f)	Cl	5	7	2	67
15	$PPh_3$ ( <b>1</b> g)	Cl	5	7	2	_[e]

[a]	Yield of the isolated product. [b] At	t 80°C. [c] N	o reaction	at 80°C.
[d]	Conversion after 0.5 h indicated in pa	rentheses. [e	] Traces.	

with entry 1 because a lower amount of gallium could be used, full conversion was reached in only 2 h, and the temperature could be lowered to 40°C. Since none of the two steps of the tandem reaction is promoted by AgSbF<sub>6</sub> alone,<sup>[25]</sup> we suppose that (IPr)GaCl<sub>2</sub><sup>+</sup> is the active species of the catalytic cycle. An excess of silver with respect to gallium increases the rate of the tandem process, probably by increasing the concentration of the monocationic gallium species rather than forming an elusive di- or tricationic gallium-centered complex (Table 1, entries 4 and 5).<sup>[26]</sup> This effect is even more spectacular when using only 1 mol% of (IPr)GaCl<sub>3</sub> (Table 1, entries 6-8). A two- or three-fold excess of AgSbF<sub>6</sub> markedly increased the yields of the tandem process (up to 96%), although the reaction time was longer. We stress that it is not possible to carry out this (or probably any other) reaction with GaCl<sub>3</sub> in such a low catalytic amount. In the rest of the screening, a 1.4-fold excess of silver was used. For instance, with 5 mol% of (IPr)GaCl<sub>3</sub> and 7 mol% of AgSbF<sub>6</sub>, the product was isolated nearly quantitatively after 2 h (Table 1, entry 9). Similar results were obtained with the bromide and iodide derivatives (Table 1, entries 10 and 11). Other (NHC)GaCl<sub>3</sub> adducts could be used, however the yields were markedly lower (Table 1, entries 12-14). As a matter of comparison, the triphenylphosphine adduct was tested but this proved inefficient (Table 1, entry 15).<sup>[27]</sup> Thus, while the peculiar selectivity of GaCl<sub>3</sub> is maintained, the (IPr)GaCl<sub>3</sub>/AgSbF<sub>6</sub> catalytic mixture is more active and the putative (IPr)GaCl<sub>2</sub><sup>+</sup> active species is less fragile.

To avoid the systematic handling of the silver additive, we next evaluated the isolated cationic species **2a-d** (Table 2). Complex **2a**, which exhibits an electron-rich nitrile, did not



Table 2. Bimolecular reaction catalyzed by isolated gallium(III) dihalides.

		OMe A + () - (3 equiv)	<b>IPr)LGaCl₂]SbF<sub>6</sub></b> gSbF <sub>6</sub> (b mol%)  DCE, 4 h, <i>T</i> °C	(a mol%) Me E	OMe
Entry	(E = CO <sub>2</sub> Me) Cat.	Т [°С]	a [mol %]	b [mol%]	Yield [%] <sup>[a]</sup>
1	2 a	40	5	0	0 <sup>[b]</sup>
2	2a	40	5	5	30
3	2 b	40	5	0	36
4	2b	40	5	5	81
5	2 c	40	5	0	81
6	2 d	40	5	0	55
7	2a	80	5	0	_[c]
8	2 b	80	5	0	79
9	2 c	80	5	0	82
10	2 d	80	5	0	72

[a] Yield of the isolated product. [b] No reaction. [c] Traces.

provide the tandem product, nor its carbocyclization precursor (Table 2, entry 1). Product 5 could be obtained nonetheless in 30% yield when using  $AgSbF_6$  as additive (Table 2, entry 2). Here, the main role of the silver salt is probably not to generate a gallium-centered dication but to abstract the nitrile itself. Pertaining to this hypothesis, we could serendipitously collect single crystals of [(2,4,6-trimethoxybenzonitrile)<sub>2</sub>Ag]SbF<sub>6</sub> and characterize them by using X-ray diffraction.<sup>[28]</sup> With the benzonitrile derivative 2b, without silver salt, we were pleased to find product 5 in the reaction mixture and isolate it in an encouraging 36% yield (Table 2, entry 3). Again, the yield could be greatly improved to 81 % with  $AgSbF_6$  (Table 2, entry 4). Of particular interest, the same yield could be reached without the silver additive when using complex 2c, which exhibits the more labile trifluorobenzonitrile ligand (Table 2, entry 5). On the other hand, the pentafluoronitrile derivative 2d gave rise to a lower yield of 55% (Table 2, entry 6). Increasing the temperature to 80°C was beneficial with 2b and 2d (Table 2, entries 8 and 10), but not with 2c, which remained the more active catalyst (Table 2, entry 9). Apart from anisole, other nucleophiles were tested and gave very good results (see the Supporting Information).

An intramolecular reaction was next investigated (Table 3). At 40 °C, the (IPr)GaCl<sub>3</sub>/AgSbF<sub>6</sub> mixture gave the best yield of the series (91%, Table 3, entry 1) and outperformed the cationic complexes **2b–d** (Table 3, entries 2–4).

Again, among the latter, 2c proved to be the most efficient (81%, Table 3, entry 3). Interestingly, at 80°C, no amelioration was observed (Table 3, entries 5, 6, and 8), except for 2c, which performed similarly to the Ga/Ag mixture (93% yield, Table 3, entry 7).

Lastly, we carried out the cyclization of enyne 8 in the presence of anisole (Scheme 2).<sup>[29]</sup> By using either the Ga/ Ag mixture or the cationic catalyst 2c in DCE at 80°C, we could isolate the regioisomers 9a and 9b from many other

Table 3. Intramolecular reaction catalyzed by isolated or in situ-generated gallium(III) dihalides.

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[a] Yield of the isolated product.

2 d

1

2

3

4

5

6

7

8



5

0

52

Scheme 2. Gallium(III)-catalyzed 1,6-enyne cyclization.

80

unidentified by-products in less than 30% yield. Gratifyingly, the selectivity could be greatly improved in toluene.<sup>[30]</sup>

In conclusion, the combination of (NHC)GaX<sub>3</sub> complexes and AgSbF<sub>6</sub> advantageously replaces hygroscopic GaX<sub>3</sub> salts. While the peculiar selectivity of the salts is maintained, the air-stable NHC adducts allow better yields at lower temperatures and faster reaction times. Catalytic amounts as low as 1 mol% can be used, which is not possible with simple gallium(III) halides. Besides, a "silver-free" protocol<sup>[31]</sup> based on the use of well-defined cationic gallium halides has been developed. The advantages of having one metal instead of two in the reaction mixture have been clearly recognized in the field of gold catalysis.<sup>[32]</sup> This paves the way for further developments in Ga<sup>III</sup> catalysis in general, and in (asymmetric)  $\pi$ -acid catalysis in particular. The synthesis of air- and moisture-stable, and yet active, cationic gallium species is also a goal actively pursued in our laboratory.

#### **Experimental Section**

General procedure (Table 2): The arenyne 4 (0.25 mmol, 1 equiv) and anisole (3 equiv) were mixed in a screw-cap vial under argon. 1,2-Dichloroethane (0.25 M) was added and the mixture was stirred for 5 min. The gallium(III) catalyst (5 mol%) was added and the mixture was stirred at 40 or 80°C for 4 h. The mixture was quenched with Et<sub>3</sub>N (1 drop). The reaction mixture was diluted with diethyl ether (10 mL). The solution was filtered on a short pad of silica, which was rinsed with dieth-

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yl ether (5 mL). After evaporation, the crude was purified by flash chromatography (92:8 cyclohexane/EtOAc).

#### Acknowledgements

This work was supported by CNRS, MESR, and UPS (Chaire d'Excellence). We thank S. E. Denmark and P. de Frémont for useful discussions.

**Keywords:** cycloisomerization • gallium • heterocyclic carbenes • homogeneous catalysis • Lewis acids

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varren, Angew. Chem. 2007, 119, 2726; Angew. Chem. Int. Ed. **2007**, *46*, 2672.

[31] Silver is needed once for the generation of the cationic species but no longer in the catalytic tests. We cannot exclude contamination by silver, however, silver is not an active catalyst here.

[32] See inter alia: S. Gaillard, J. Bosson, R. S. Ramón, P. Nun, A. M. Z. Slawin, S. P. Nolan, Chem. Eur. J. 2010, 16, 13729, and the references therein.

Received: April 9, 2012 Published online:

5 These are not the final page numbers! 77

### HEMISTRY

A EUROPEAN JOURNAL

#### **Gallium Catalysis**

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Cationic Gallium(III) Halide Complexes: a New Generation of  $\pi$ -Lewis Acids



active mixture

Ga-neration X: Well-defined neutral and cationic gallium(III) halide complexes have been synthesized and evaluated in catalysis. Both the (NHC)GaX<sub>3</sub>/AgSbF<sub>6</sub> catalytic mixture and isolated (NHC) $GaX_2^+$  species function as exquisite  $\pi$ -Lewis acids in

typical GaX<sub>3</sub>-catalyzed reactions (see scheme). The cationic complexes are more active than  $GaX_3$  and yet more resistant to hydrolysis, which allows lower catalytic loadings and faster reactions.