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Catalytic Use of Low-Valent Cationic Gallium(I) Complexes as π-Acids

Zhilong Li,[a] Guillaume Thiery,[a] Martin R. Lichtenthaler,[b,c] Régis Guillot,[a] Ingo Krossing,[c] Vincent Gandon,[a,]* and Christophe Bour[a,]*

[a] Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Université Paris-Sud, Université Paris-Saclay, Bâtiment 420, 91405 Orsay cedex, France
Phone: (+33)169157651
E-mail: christophe.bour@u-psud.fr, vincent.gandon@u-psud.fr
[b] Department of Chemistry, University of California, Berkeley, USA
[c] Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany

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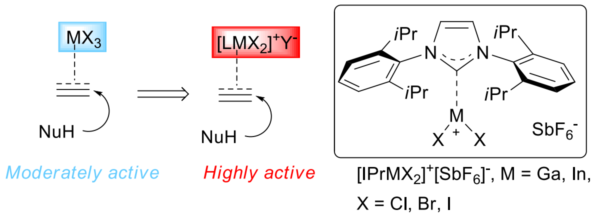
Abstract. Transformations of alkene and alkyne substrates relevant to π-Lewis acid catalysis have been performed using low-valent Ga(I) species for the first time. $[Ga(I)(PhF)_2]^+[Al(OR^F)_4]^-$ and gallium dichloride (i.e. $[Ga(I)]^+[GaCl_4]^-$) proved to be efficient catalysts for cycloisomerizations, Friedel-Crafts reactions, transfer hydrogenations, and reductive hydroarylations. Their activity is compared to more common Ga(III) complexes. This study shows that even the readily available and yet overlooked gallium dichloride salt can be a more active π-Lewis acid catalyst than gallium trichloride or other Ga(III) species.

Keywords: Alkenes; Alkynes; Gallium; Homogeneous catalysis; Low-valent species; π-Lewis acids.

Salts of Group 13 metals such as GaX_3 and InX_3 are increasingly used in homogeneous catalysis to promote the formation of C-C, C-X, and C-H bonds.[1] This renewed interest can be notably explained by the recent discovery of their ability to catalyze nucleophilic additions across C-C π-bonds.[2,3] This reactivity of π-Lewis acids was traditionally believed to be the prerogative of late transition metals such as Ru, Rh, Ir, Pt or Au, but it is now established that alkynes, alkenes and allenes can be also activated by soft main group metals.[4] In spite of encouraging results obtained in this area with gallium and indium complexes, functional group tolerance remains an issue, so it is still necessary to develop and screen new catalysts,[5] or to test existing species that have not been considered as π-Lewis acids. In that respect, we have recently demonstrated that cationic species of type $LGaX_2^+$ or $LInX_2^+$, where L is a N-heterocyclic carbene (NHC) such as IPr, have a higher stability and are more active and selective than the corresponding GaX_3 and InX_3 salts (Scheme 1).[6,7] Nevertheless, these complexes remain able to cleave some C*sp*^{3}-O bonds (e.g. deprotection of Ar-OMe or acetal groups) and are incompatible with nitro groups.



Scheme 1. Ga(III) and In(III) complexes used as π-Lewis acids.

Another way to modulate the activity would be to play on the oxidation state of the metal. This approach is well-established in gold catalysis, where Au(I) and Au(III) species can lead to different reaction outcomes.[8] In contrast with Ga(III)- and In(III)-based catalysts, Ga(I) complexes have remained little exploited in homogeneous molecular catalysis. Unlike low-valent In(I) salts used in a wide range of organic transformations as catalysts (e.g. InX-catalyzed allylations,[9] allenylation,[9] propargylations,[9] Reformatsky reactions,[10] 1,2-additions[11] or radical cyclizations[12]), the use of Ga(I) has been mainly limited to stoichiometric reactions,[13] with a notable recent exception for the formation of C-C bonds from boron-based pronucleophiles and various electrophiles.[14] The in situ generated [18]-crown-6–Ga(I)·$(dioxane)_n$OTf complex was used for its ambiphilic nature, since Ga(I) is both a Lewis acid[15] (by its three vacant p orbitals) and a Lewis base[16] (by its lone pair). Nevertheless, in this study and others related to

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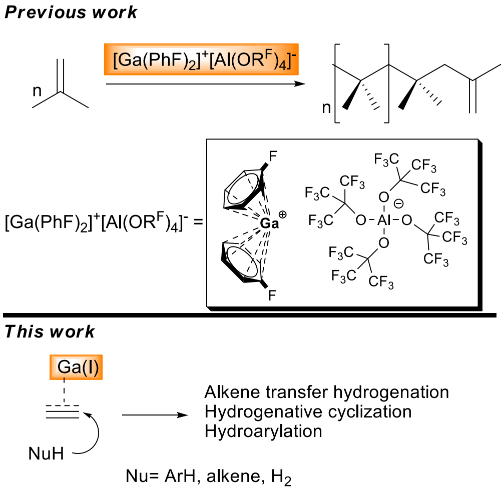
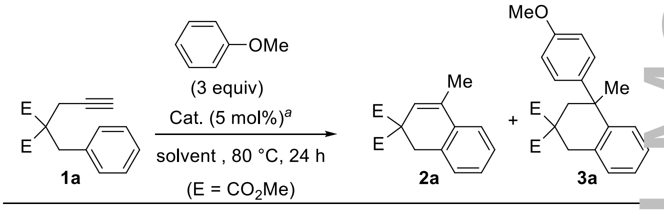
molecular catalysis, it is mostly the σ-Lewis acidity that has been exploited, i.e. the catalytic activation of C-X bonds (X = N, O, Cl, Br). A Clue that Ga(I) species could be employed as π-Lewis acid for applications in molecular catalysis actually comes from the activation of allylboron substrates by vertical neighboring In(I) species.[9b,17] Another clue comes from polymer chemistry, since low-valent univalent cationic complexes of type $[Ga(I)(PhF)_2]^+[Al(OR^F)_4]^-$ ($R^F= C(CF_3)_3$) can activate isobutylene towards the formation of highly reactive polyisobutylene (HR-PIB, Scheme 2).[18] Herein, we report the first use of Ga(I) complexes as π-acid catalysts for molecular applications.



Scheme 2. Activation of C-C π bonds by Ga(I) complexes.

We started our investigation with a benchmark reaction that we have used previously to evaluate the ability of Ga(III) Lewis acids to activate alkynes and alkenes using a single substrate (Table 1).[2a,2h] The cycloisomerization of arenyne **1a** can lead to the dihydronaphthalene derivative **2a** which, in the presence of a nucleophile such as anisole, can give rise to the tetrahydronaphthalene **3a**.[6] In a preceding study,[Fehler! Textmarke nicht definiert.a] we found that $[IPrGaCl_2]^+[SbF_6]^-$ catalyzes the selective transformation of **1a** into **3a** in 1,2-dichloroethane (DCE) (entry 1) or toluene (entry 2) at 80 °C. In DCE at 80 °C, we were pleased to see that $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ could also be used as catalyst to give **2a** in 91% yield (entry 3). However, in contrast with $[IPrGaCl_2]^+[SbF_6]^-$, the formation of **3a** was very slow. Gratifyingly, **3a** could be obtained selectively in toluene in 81% yield (entry 4). Importantly, *NMR studies revealed that $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ was not subject to disproportionation under the reaction conditions* (see the Supporting Information). Since the Ga(III) and the Ga(I) complexes have different counterions, $[IPrGaCl_2]^+[Al(OR^F)_4]^-$ was also tested. Even though $[Al(OR^F)_4]^-$ is an even weaker coordinating anion than $[SbF_6]^-$,[19] $[IPrGaCl_2]^+[Al(OR^F)_4]^-$ actually seemed less reactive than $[IPrGaCl_2]^+[SbF_6]^-$ as it could not promote the addition of anisole in both DCE or toluene (entries 5 and 6). This could be due to a faster hydrolysis of the former by adventitious water under such reaction conditions, as a small amount of the cationic gallium dihydroxide $[\{IPrGaCl(\mu\text{-}OH)_2\}_2\cdot H_2O]^{2+}\{[Al(OR^F)_4]^-\}_2$ could be isolated and characterized by X-ray diffraction.[20] The corresponding silver salts $Ag^+[SbF_6]^-$ and $[Ag(DCM)_3]^+[Al(OR^F)_4]^-$ (DCM = dichloromethane) [9a] proved inactive (entries 7 and 8). With the Ga(I)-containing salt "GaI",[21] **2a** was obtained selectively (entries 9 and 10). In toluene, Ga_2Cl_4[22] led to **2a** (entry 11), but **3a** was obtained as the major product in DCE (entry 12). This is in sharp contrast with $GaCl_3$, with which **3a** was a minor product (entry 13).[23] On the other hand, the use of $GaCl_3$ and $[Ag(DCM)_3]^+[Al(OR^F)_4]^-$ to form the putative highly electrophilic $[GaCl_2]^+[Al(OR^F)_4]^-$ species, provided **3a** in both DCE and toluene (entry 14-15).

Table 1. Reaction optimization for Ga-catalyzed dihydroarylation of arenyne **1a** with anisole.



Entry	Cat.	Solvent	Yield of **2a** [%]^b	Yield of **3a** [%]^b
1	$[IPrGaCl_2]^+[SbF_6]^{-\,c}$	DCE	-	92
2	$[IPrGaCl_2]^+[SbF_6]^{-\,c}$	toluene	-	95
3	$[Ga(PhF)_2]^+[Al(OR^F)_4]^-$	DCE	91	5
4	$[Ga(PhF)_2]^+[Al(OR^F)_4]^-$	toluene	0	81
5	$[IPrGaCl_2]^+[Al(OR^F)_4]^{-\,c}$	DCE	90	0
6	$[IPrGaCl_2]^+[Al(OR^F)_4]^{-\,c}$	toluene	89	0
7	$Ag^+[SbF_6]^-$	DCE	NR	-
8	$[Ag(DCM)_3]^+[Al(OR^F)_4]^-$	DCE	NR	-
9	GaI^d	DCE	99	-
10	GaI^d	toluene	98	-
11	Ga_2Cl_4	toluene	79	11
12	Ga_2Cl_4	DCE	15	77
13	$GaCl_3$	DCE	77	14
14	$[GaCl_2]^+[Al(OR^F)_4]^{-\,e}$	DCE	-	56
15	$[GaCl_2]^+[Al(OR^F)_4]^{-\,e}$	toluene	-	80

[a] Reaction conditions: 1,6-arenyne **1a** and anisole (3 equiv) in the indicated solvent (0.2 M) in the presence of catalyst at the indicated temperature for 24 h. [b] Isolated yields. [c] Generated in situ by using $IPrGaCl_3$ and $Ag^+[SbF_6]^-$ or $[Ag(DCM)_3]^+[Al(OR^F)_4]^-$. [d] 20 mol%. [e] Generated in situ by using $GaCl_3$ and $[Ag(DCM)_3]^+[Al(OR^F)_4]^-$

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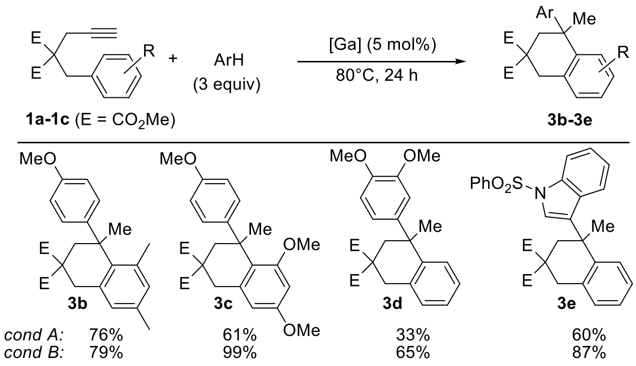
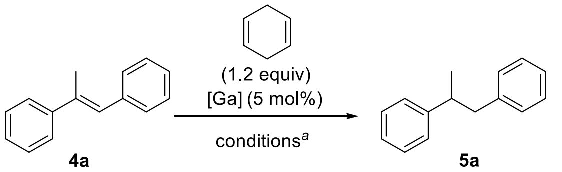
Given the good activity of $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ in toluene and Ga_2Cl_4 in DCE for the dihydroarylation of **1a**, various 1,6-arenynes and aromatic nucleophiles were then tested (Scheme 3). The corresponding dihydroarylation products were isolated in good to excellent yields. The results obtained with Ga_2Cl_4 are markedly better for **3c-e**.



Scheme 3. Bimolecular dihydroarylation of 1,6-arenynes with aromatics. *Conditions A*: [Ga] = $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ in toluene; *Conditions B*: [Ga] = Ga_2Cl_4 in DCE.

The use of $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ and Ga_2Cl_4 as catalysts was then extended to transfer hydrogenation of alkenes,[24] using 1,4-cyclohexadiene (1,4-CHD) as dihydrogen source.[25] We started this study with the reduction of 1,2-diphenylpropene **4a** (Table 2). At 80 °C in DCE, the reduction was efficient with $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ (entry 1), but sluggish with Ga_2Cl_4 (entry 2). With the latter, the yield increased significantly in toluene (entry 3). Raising the temperature to 110 °C improved the yield to 94% with Ga_2Cl_4 (entry 4) and to 73% with $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ (entry 5).

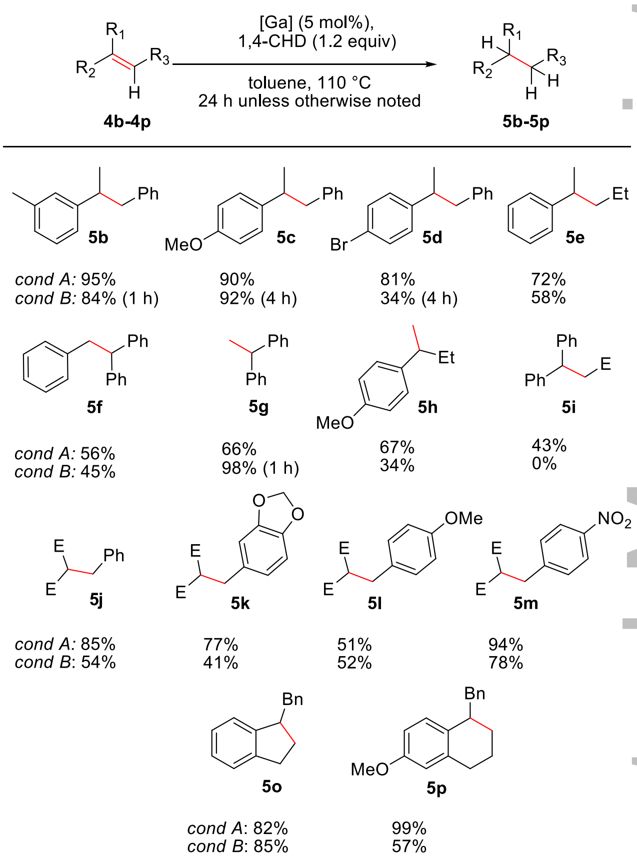
Table 2. Reaction optimization for Ga(I)-catalyzed transfer hydrogenation of (*E*)-1,2-diphenylpropene **4a**.



Entry	[Ga]	Solvent	T [°C]	Yield of **5a** [%]^b
1	$[Ga(PhF)_2]^+[Al(OR^F)_4]^-$	DCE	80	61
2	Ga_2Cl_4	DCE	80	37
3	Ga_2Cl_4	toluene	80	61
4	Ga_2Cl_4	toluene	110	94
5	$[Ga(PhF)_2]^+[Al(OR^F)_4]^-$	toluene	110	73

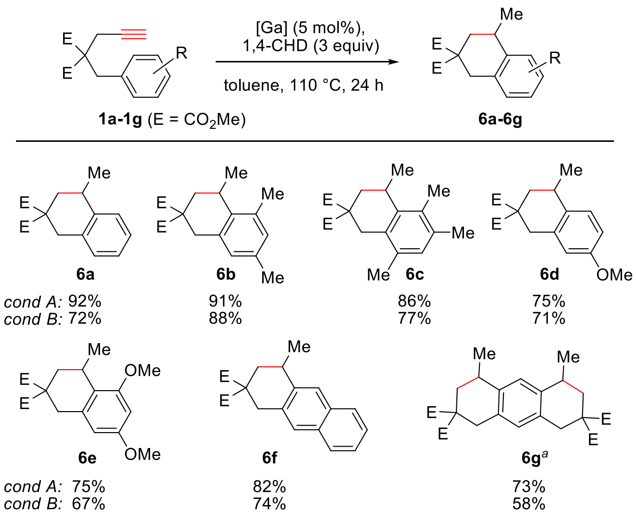
[a] Reactions conditions: **4a** (1 equiv) and 1,4-CHD (1.2 equiv) in the indicated solvent (0.2 M) in the presence of the catalyst (5 mol%) for 24 h. [b] Isolated yields.

With these optimal reaction conditions, we explored the scope of the Ga(I)-catalyzed transfer hydrogenation (Scheme 4). A range of di- or trisubstituted acyclic or cyclic alkenes were hydrogenated in good to high yields. With a few exceptions (**5c**, **5g**, **5l**, **5n**), $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ proved more efficient than Ga_2Cl_4. Remarkably, methoxy, and nitro groups were not affected by these conditions (**5j-5m**). Again, these Ga(I) species proved superior to $GaCl_3$. For instance, whereas the nitro derivative **5m** was obtained in 94% and 78% yield with $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ and Ga_2Cl_4 respectively, $GaCl_3$ furnished it in 45% yield only.



Scheme 4. Scope of the Ga(I)-catalyzed transfer hydrogenation of alkenes. *Conditions A*: [Ga] = $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$; *Conditions B*: [Ga] = Ga_2Cl_4. PMP = *para*-methoxyphenyl; PNP = *para*-nitrophenyl.

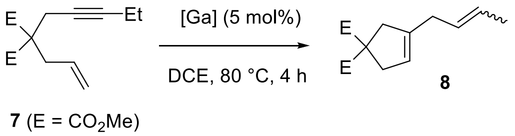
We next investigated the potential of the Ga(I) complexes in hydrogenative cyclizations (Scheme 5).[Fehler! Textmarke nicht definiert.a] Again, $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ and Ga_2Cl_4 proved to be catalytically active. The cyclization/reduction products were isolated in good to high yields. Again, $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ led to better yields than Ga_2Cl_4.



Scheme 5. Ga(I)-catalyzed hydrogenative cyclizations of arenyne. *Conditions A*: [Ga] = $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$; *Conditions B*: [Ga] = Ga_2Cl_4. [a] 6 equiv of 1,4-CHD; *dl* : *meso* = 1/1 .

Lastly, we briefly investigated the cycloisomerization of enyne **7** (Table 3).[Fehler! Textmarke nicht definiert.e,Fehler! Textmarke nicht definiert.,26] This reaction is highly challenging since Ga(III) species tend to encourage the polymerization of the substrate. With $GaCl_3$ and $[IPrGaCl_2]^+[Al(OR^F)_4]^-$, **8** was obtained in a low 17% and 32% yield respectively (entries 1 and 2, full conversion but high level of polymerization).[27] With $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$, the yield increased to 45% (entry 3), and reached 60% with Ga_2Cl_4 (entry 4).

Table 3. Ga(I)-catalyzed cycloisomerisation of enyne **7**.



Entry	[Ga]	*E/Z*	Yield(%)[a]
1	$GaCl_3$	3/2	17
2	$[IPrGaCl_2]^+[Al(OR^F)_4]^{-b}$	8/1	32
3	$[Ga(PhF)_2]^+[Al(OR^F)_4]^-$	3/2	45
4	Ga_2Cl_4	2/1	60

[a] Isolated yields, full conversion reached in each case. [b] Generated in situ by using $IPrGaCl_3$ and $[Ag(DCM)_3]^+[Al(OR^F)_4]^-$.

In conclusion, we have developed the first catalytic use of cationic Ga(I) species in homogeneous molecular π-acid catalysis. Compared to other cationic Ga(III) complexes in hydroarylation, hydrogenative cyclization or alkene transfer hydrogenation, the activity of $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ and Ga_2Cl_4 is competitive or markedly superior. Moreover, functional groups that are typically incompatible with $GaCl_3$ or other Ga(III) species proved compatible with these soft Ga(I)-based catalysts.

Experimental Section

General procedure for Ga(I)-catalyzed transfer hydrogenation (Scheme 4). Under argon, the alkene (0.25 mmol, 1 equiv) was introduced into a glass tube containing a magnetic stirrer. The catalyst (5 mol%, 0.0125 mmol) and then dry degassed solvent ($0.25\ mol.L^{-1}$) were added into the reaction vessel. The tube was capped with a rubber septum. 1,4-CHD (0.3 mmol, 30 μL, 1.2 equiv) was added through the septum with a Hamilton® syringe. The mixture was then heated at 110 °C and the reaction progress was monitored by GC. After completion, the reaction mixture was filtered over a pad of celite, which was rinsed with DCM or Et_2O. Volatiles were removed by rotary evaporation under vacuum. The crude was purified by flash column chromatography on silica gel (eluent: cyclohexane/ethyl acetate).

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UPDATE

Catalytic Use of Low-Valent Cationic Gallium(I) Complexes as π-Acids

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Zhilong Li, Guillaume Thiery, Martin R. Lichtenthaler, Régis Guillot, Ingo Krossing, Vincent Gandon,* Christophe Bour*