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A Discrete N,O,N-Supported Gallium Amido Complex for the Intermolecular Hydroamination of Terminal Alkynes

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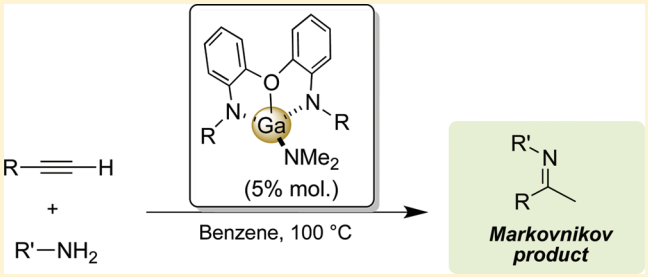
Supporting Information

ABSTRACT: The diamino-ether ligand $\{(C_5H_9)NH\text{-}C_6H_4\}_2O$ (**1**) was found to readily react with 0.5 equiv of $Ga_2(NMe_2)_6$ via an amine elimination route to afford the N,O,N-supported Ga amido species $\{\eta^3\text{-}N,O,N\text{-}((C_5H_9)N\text{-}C_6H_4)_2O\}GaNMe_2$ (**2**) in a reasonable yield (51%). As determined by X-ray crystallography, the four-coordinate Ga center in **2** adopts an unusual trigonal-monopyramidal geometry. Compound **2** effectively catalyzes the hydroamination of terminal alkynes (such as 1-hexyne and phenylacetylene) in the presence of primary amines (aniline and butylamine). Kinetic studies on the latter catalytic reactions suggest that these proceed with a first-order rate dependence on alkyne and on species **2**. In preliminary studies aiming at the isolation of intermediates relevant to the present catalysis, the dimeric Ga complex $[\{\eta^2\text{-}N,N\text{-}((C_5H_9)N\text{-}C_6H_4)_2O\}Ga(\mu\text{-}NHPh)]_2$ (**3**) was synthesized by an aminolysis reaction between compound **2** and aniline; its identity was confirmed by X-ray crystallographic analysis.



INTRODUCTION

Well-defined group 13 organo compounds supported by various N- and/or O-based multidentate chelating ligands, such as, for instance, salen- and salan-derived ligands, have been widely studied and have found numerous applications in homogeneous catalysis ranging from their use in the mediation of various Lewis acid assisted organic reactions to that in polymerization catalysis of polar monomers (cyclic esters, epoxides).[1−3] Efficient discrete group 13 based catalysts developed thus far mainly consist of five-coordinate or higher species of the type $(L_2X_2)MX'$ or $(L_2X_2)M(X')(L')$.[1] Indeed, in such complexes, the high coordination of the metal center and the formation of robust $(L_2X_2)M$ chelates typically ensure an excellent stability and disfavor the formation of undesirable aggregates. Despite their being usually quite reactive and thus of interest in catalysis, well-defined low-coordinate (<4) group 13 species have thus far found very few applications in the latter area, which is certainly related to their limited stability (in polar and/or protic medium, for instance).[4] In addition, the well-known propensity of such electrophilic species toward aggregate formation (through diverse binding/bridging modes) often complicates their coordination chemistry and their isolation in a pure form.

Tetracoordinate Al(III) complexes supported by an appropriately designed N,N,N-dianionic ligand forcing the metal center in a trigonal-monopyramidal coordination geometry (versus its classically preferred tetrahedral geometry) have been shown to be effective Lewis acid catalysts for the mediation of several asymmetric transformations.[5] More recently, we reported on the use of distorted N,O,N-supported Al species for the highly active and controlled ring-opening polymerization of cyclic carbonates.[6] The increased reactivity of such group 13 complexes arises from a destabilizing ligand-defined geometry distortion, resulting in a more Lewis acidic Al metal center.[5c] In comparison to "classical" low-coordinate (two- and three-coordinate) group 13 species, distorted $(LX_2)AlX'$-type compounds may be readily accessible (in a mononuclear form) and provide a superior steric protection of the Lewis acidic metal center and, hence, an increased stability. Such entities may thus well represent a reasonable reactivity/stability balance, rendering them suitable for catalysis and, possibly, for novel reactivity in group 13 chemistry.

On this basis and aiming at the development of novel group 13 mediated reactions, we have become interested in probing the potential usefulness of distorted (NON)MX′-type species (M = group 13 metal) as catalysts for the intermolecular hydroamination of alkynes, a widely studied atom-efficient process for the formation of imines and enamines from alkynes and primary amines.[7] However, while various and numerous metal-based catalysts have been shown to mediate the latter transformation,[7] no group 13 catalyst had been reported when the present work was initiated.[8] Studies in this area have been thus far restricted to a couple of reports on aluminum-mediated intramolecular hydroamination of alkenes, found to proceed under rather harsh conditions.[9]

As shown below, initial studies on alkyne hydroamination using N,O,N-supported Al amido species were unsuccessful.

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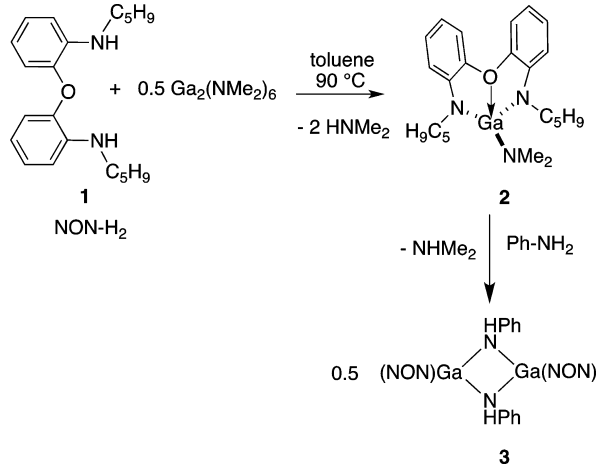
As simple Ga(III) precursors such as $GaCl_3$ have been shown, in some instances, to readily activate alkynes,[1,10] we were prompted to extend our investigations to the Ga analogues. Here we report on the synthesis and structural characterization of a distorted N,O,N-supported Ga amido complex and its subsequent use in alkyne hydroamination catalysis. Kinetic studies of the latter catalytic reaction are also provided and briefly discussed.

RESULTS AND DISCUSSION

N,O,N-Supported Ga Amido Complex (NON)Ga(NMe$_2$) (2). As illustrated in Scheme 1, the N,O,N-supported Ga amido species $\{\eta^3$-*N,O,N*-$((C_5H_9)N\text{-}C_6H_4)_2O\}GaNMe_2$ (**2**) may be directly prepared in a reasonable yield (51%) via an amine elimination route by reaction of the diamino-ether ligand **1** with 0.5 equiv of $Ga_2(NMe_2)_6$. Compound **2** was isolated as an air- and moisture-sensitive colorless solid, and its molecular structure was confirmed by X-ray crystallography analysis.

Scheme 1



As depicted in Figure 1, complex **2** indeed consists of a four-coordinate Ga species effectively η^3-N,O,N-chelated by the bis-amido-ether $\{((C_5H_9)N\text{-}C_6H_4)_2O\}^{2-}$ dianionic ligand, with the Ga metal center adopting an unusual distorted-trigonal-monopyramidal (tmp) geometry. The nitrogens of the three amido groups (defining the pyramidal base) are thus nearly coplanar with Ga (sum of N−Ga−N angles 358.72°). The bonding parameters in **2** are essentially as expected (see Figure 1) with, in particular, the Ga(1)−N(1) and Ga(1)−N(2) amido bond distances (1.877(2) and 1.891(2) Å, respectively) lying in the lower range (1.85−2.05 Å) for terminal Ga−amido bonds.[11] Notably, the Ga(1)−N(3) bond distance (1.816(2) Å) is significantly shorter, which most likely reflects the ionic contraction of the Ga(1) and N(3) radii due to the polar character of the latter bond.[12] Importantly, the solid-state data for **2** indicate the presence of an apical vacant site ideally disposed for coordination to the Lewis acid Ga center. From a structural point of view, the Ga species **2** represents the first X-ray characterized compound in which a four-coordinated Ga center adopts a clear-cut tmp geometry. As for its solution structure, NMR data for **2** are consistent with a C_s-symmetric structure under the studied conditions (C_6D_6, room temperature), in agreement with solid-state structural data.

As stated in the introduction, the hydroamination of alkynes was first tested using Al derivatives. More specifically, the previously reported Al complexes $\{RN\text{-}C_6H_4\}_2OAlNMe_2$ (R = C_5H_9, C_6H_{11}),[6] which are isostructural with the Ga compound **2**, were used and found to be essentially inactive in the intermolecular hydroamination of alkynes under the studied conditions. Thus, using various primary amines and terminal alkyne substrates, only trace amounts of hydroamination products were observed under harsh reaction conditions (at best 7% conversion to the Markovnikov hydroamination product, 1-hexyne and aniline as substrates, 10 mol % Al species $\{(C_5H_9)N\text{-}C_6H_4\}_2OAlNMe_2$, C_6D_6, 150 °C, 65 h). In contrast, as summarized in Table 1, the Ga species **2** (using 5 or 10% mol of **2** versus substrates, C_6D_6, 100 °C) effectively catalyzes the

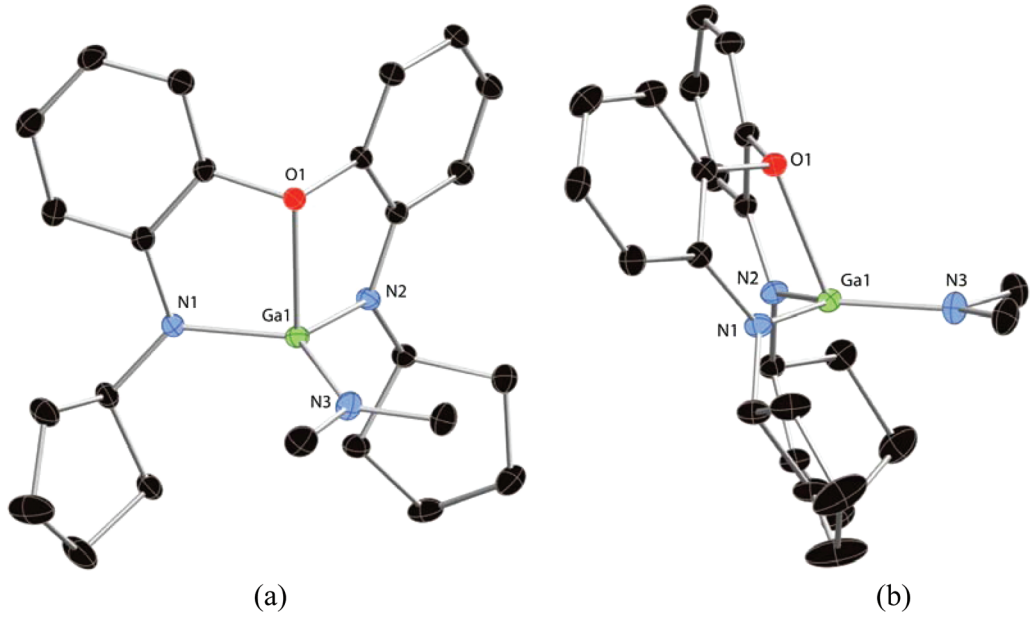


Figure 1. Molecular structure of the Ga amido species **2** (Ortep view). The hydrogens are omitted for clarity: (a) front view; (b) side view. Selected bond distances (Å): Ga(1)−N(1) = 1.877(2), Ga(1)−N(2) = 1.891(2), Ga(1)−N(3) = 1.816(2), Ga(1)−O(1) = 2.1241(16). Selected bond angles (deg): N(3)−Ga(1)−N(1) = 119.16(10), N(3)−Ga(1)−N(2) = 117.92(9), N(1)−Ga(1)−N(2) = 121.67(9), N(2)−Ga(1)−O(1) = 82.92(7).

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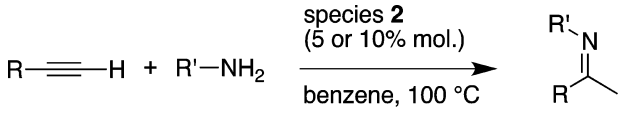
Table 1. Gallium-Catalyzed Hydroamination of Terminal Alkynes[a]



entry	alkyne	amine	t (h)	conversn (%)[b]
1	1-hexyne	aniline	17	90
2[c]	1-hexyne	aniline	24	52
3[d]	1-hexyne	aniline	65	15
4[e]	1-hexyne	aniline	65	26
5[f]	1-hexyne	butylamine	24	48
6[f]	1-hexyne	^{t}Bu-NH$_2$	24	<5
7	Ph-acetylene	aniline	20	22
8[g]	Ph-acetylene	aniline	7	100
9[g]	Ph-acetylene	aniline	1	40

[a]Conditions (unless indicated otherwise): 5 mol % of compound **2**, benzene, 100 °C, $[\text{alkyne}]_0 = [\text{amine}]_0 = 0.5$ M. C_6Me_6 was used as an internal standard. [b]As determined by ^{1}H NMR after hydrolysis of the reaction mixture. [c]$[\text{alkyne}]_0 = [\text{amine}]_0 = 0.156$ M. [d]2.5 mol % of $Ga_2(NMe_2)_6$ was used as a catalyst with $[\text{alkyne}]_0 = [\text{amine}]_0 = 0.156$ M. [e]5 mol % of $GaCl_3$ was used as a catalyst with $[\text{alkyne}]_0 = [\text{amine}]_0 = 0.156$ M. [f]The reaction was run at 130 °C using 10 mol % of **2**. [g]10 mol % of catalyst **2** was used.

hydroamination of terminal alkynes such as 1-hexyne and phenylacetylene whether an aryl amine (aniline) or an alkyl amine (butylamine) is used. The highest catalytic activity for species **2** is observed for the hydroamination of 1-hexyne by aniline (entries 1 and 2, Table 1): the activities are significantly lower when either phenylacetylene or butylamine is used as an alkyne or an amine source, respectively (entry 7 vs 1, entry 5 vs 1, Table 1). In all cases, as determined by NMR, only the Markovnikov product is formed (>99%), thus showing that the present catalysis proceeds with high regioselectivity. Notably, while the use of a sterically bulky primary amine substrate may be beneficial to the catalytic activity in some group 4 mediated hydroamination reactions,[7,13] the hydroamination reaction (of 1-hexyne) does not proceed using ^{t}BuNH$_2$ as an amine source (entry 6, Table 1), thus indicating that, in the present case, steric bulk may be detrimental. Finally, as a comparison, simple Ga(III) precursors such as $GaCl_3$ and $Ga_2(NMe_2)_6$ were tested as catalysts and also found to mediate the hydroamination of 1-hexene by aniline (entries 3 and 4, Table 1), albeit with an activity much lower than that of the N,O, N-supported Ga species **2**. Species **2** is less likely than $GaCl_3$ and dimer $Ga_2(NMe_2)_6$ to form robust and catalytically inactive aggregates, which may account for its higher catalytic activity in hydroamination.

To gain insight into the present Ga-catalyzed hydroamination reaction, kinetic studies were performed using 1-hexyne and aniline as substrates. As depicted in Figure 2, these data agree with an apparent first-order reaction in substrate ($k_{obs} \approx 0.03$ h^{-1} under the studied conditions). In addition, the reaction was studied at different concentrations of catalyst **2**, yielding the observation of a linear correlation between [**2**] and k_{obs} (Figure 3). In contrast, the concentration in amine (10, 20, and 30 equiv) apparently does not affect the reaction rate (Figure 4). Altogether, these kinetic data agree with the present Ga-catalyzed hydroamination being of first-order rate dependence in alkyne as well as in catalyst **2** while being of zero-order in amine. As a comparison, it may be noted that various kinetic studies on group 4 mediated hydroamination of

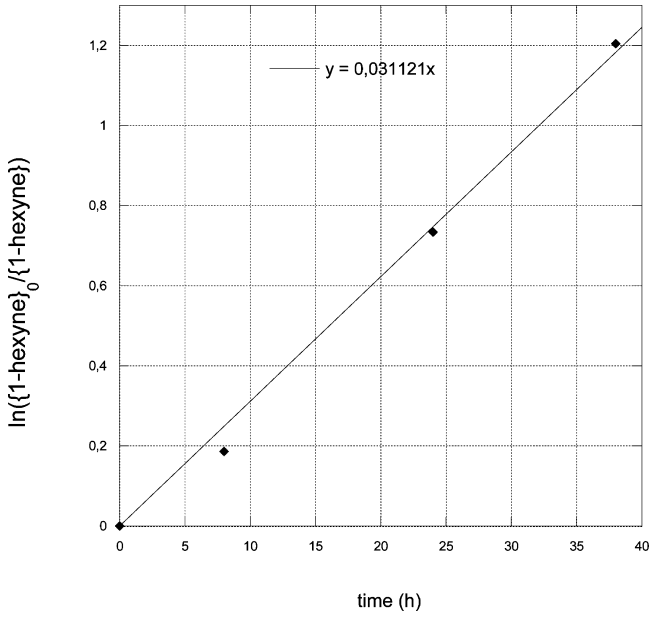


Figure 2. Plot of $\ln([\text{1-hexyne}]_0/[\text{1-hexyne}])$ versus time (h) for the hydroamination reaction of 1-hexene by aniline catalyzed by the Ga species **2**. Conditions: $[\text{1-hexene}]_0 = [\text{aniline}]_0 = 0.156$ M, 5 mol % of Ga species **2**, C_6D_6, 100 °C.

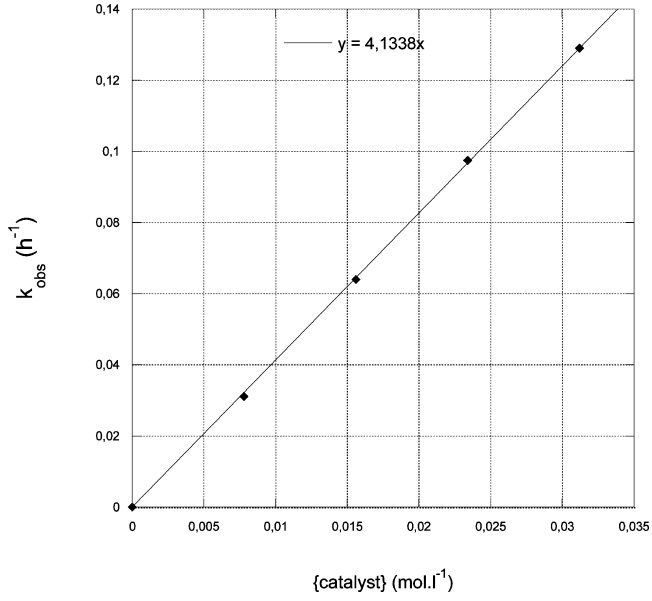


Figure 3. Plot of k_{obs} versus Ga species **2** concentration. Conditions: $[\text{1-hexyne}]_0 = [\text{aniline}]_0 = 0.156$ M, C_6D_6, 100 °C.

alkynes showed a rate dependence on amine concentration.[7,14] While being less active than Cp_2TiMe_2,[15] the hydroamination activity of Ga complex **2** is comparable, for instance, to those of the Ti species $(\eta^5\text{-Cp}^*)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}{=}\text{CSiMe}_3)$ and the Ta alkyl imido species $(Me_3CCH_2)_3Ta{=}N^tBu$.[16]

With the intent to identify (and possibly isolate) key intermediates relevant to the present hydroamination catalysis, stoichiometric reactions of 1-hexyne or/and aniline with 1 equiv of Ga species **2** were run and afforded in all but one case an intractable mixture of products. Thus, the aminolysis reaction between the Ga complex **2** and 1 equiv of aniline (toluene, 100 °C, 1 h) allows the formation of the corresponding Ga-NHPh complex $[\{\eta^2\text{-}N,N\text{-}((C_5H_9)N\text{-}C_6H_4)_2O\}\text{Ga}(\mu\text{-NHPh})]_2$

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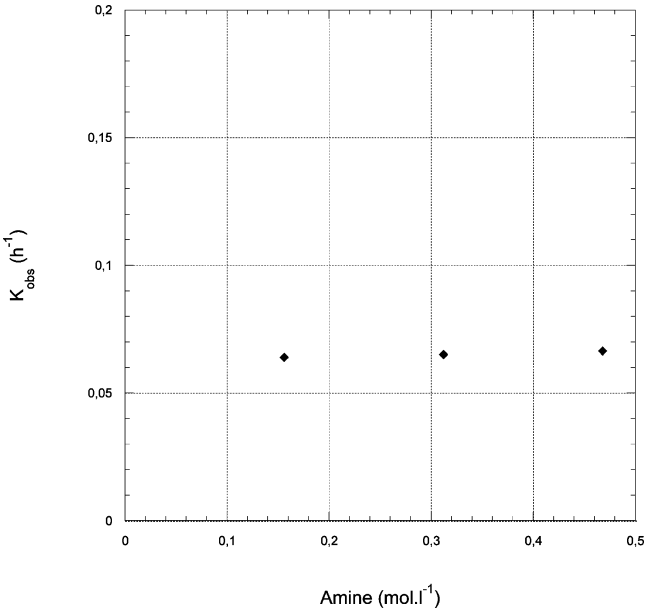

Figure 4. Plot of k_{obs} versus amine concentration for the hydroamination reaction of 1-hexene by aniline catalyzed by the Ga species **2**. Conditions: $[1\text{-hexyne}]_0$ = 0.156 M, 5 mol % of Ga species **2**, C_6D_6, 100 °C.

(**3**; Scheme 1), which was isolated as a colorless powder in a moderate yield. As deduced from X-ray crystallographic studies, complex **3** crystallizes as a centrosymmetric dimer and its molecular structure may be described as two $\{\eta^2\text{-}N,N\text{-}((C_5H_9)N\text{-}C_6H_4)_2O\}$Ga moieties being bonded to one another via two μ-NHPh amido units (Figure 5). These two amido groups are disposed in a trans configuration relative to the nearly planar Ga_2N_2 core. The centrosymmetric dimer **3** (with an inversion center located within the Ga_2N_2 core) features two four-coordinate Ga centers, each adopting a slightly distorted tetrahedral geometry. Notably and unlike species **2**, the central N,*O*,N oxygen of the chelating ligand is not coordinated to the Ga center in compound **3**. All geometrical and bonding parameters are overall rather as expected (Figure 5). In solution, the NMR data (C_6D_6, room temperature) are consistent with an effective C_i-symmetric structure and thus with the solid-state structure being retained in solution.

As deduced from a high-temperature NMR-scale monitoring experiment, the formation of compound **3** from species **2** and aniline is quantitative at 100 °C in C_6D_6 within 5 min, thus suggesting that Ga-NHPh amido species may readily form under (hydroamination) catalytic conditions. Nevertheless, monitoring a NMR-scale hydroamination of 1-hexyne by aniline using either complex **2** or **3** as catalyst (20 mol % of Ga species **2** or **3** vs substrates, 100 °C, C_6D_6) showed that both Ga species are not stable under catalytic conditions and readily undergo protonolysis: only ^{1}H NMR signals for as yet unidentified Ga derivatives and for the free ligand $\{(C_5H_9)\text{-}NH\text{-}C_6H_4\}_2O$ are observed as the catalysis proceeds. Of relevance to the subject, it should be noted that the thermolysis of related Ga amido derivatives such as $R'_2Ga(\mu\text{-}NHR)_2GaR'_2$ complexes (R, R′ = alkyl, aryl) has been reported to afford various polynuclear Ga amido imido/imido species.[17] Although further studies are clearly required, the possible formation of

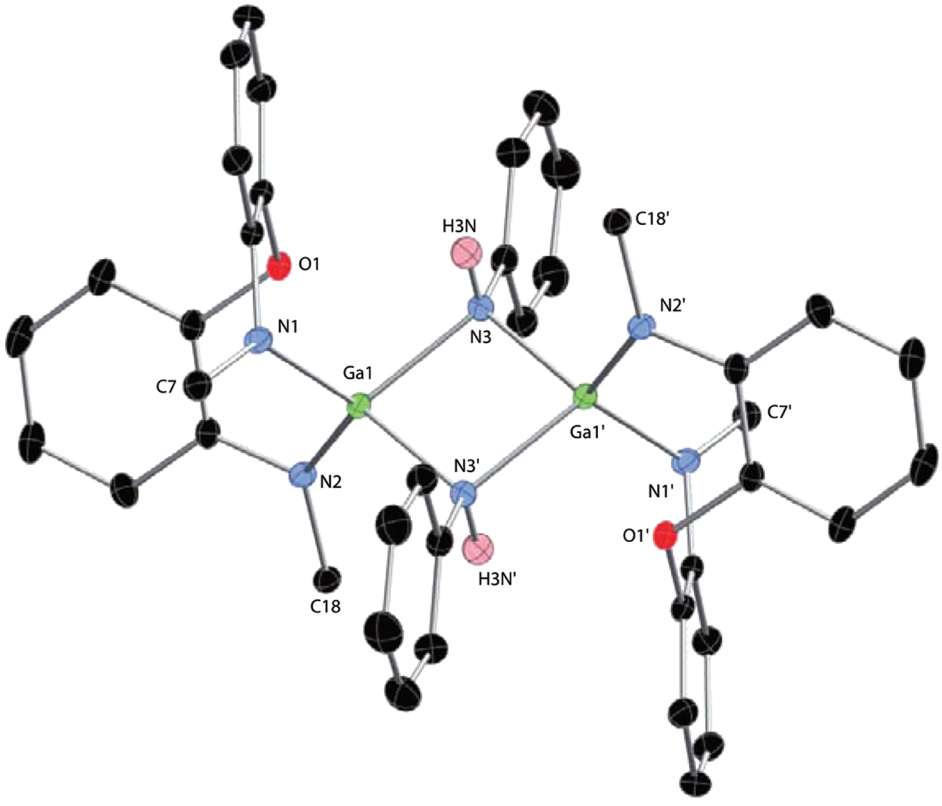

Figure 5. Molecular structure of the dimeric Ga amido species **3** (Ortep view). The hydrogens are omitted for clarity (except the N*H* groups). The C_5H_9 groups are also partially omitted for clarity: only the nitrogen-bound carbons are represented. Selected bond distances (Å): Ga(1)–N(1) = 1.900(2), Ga(1)–N(2) = 1.887(2), Ga(1)–N(3) = 2.027(2), Ga(1)–N(3)′ = 2.035(1). Selected bond angles (deg): N(2)–Ga(1)–N(1) = 113.92(9), N(2)–Ga(1)–N(3) = 120.84(9), N(1)–Ga(1)–N(3) = 114.47(9).

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such Ga amido imido/imido species may be involved in these Ga-mediated hydroamination reactions.

In summary, the diamino-ether ligand $\{(C_5H_9)NH\text{-}C_6H_4\}_2O$ may readily react with $Ga_2(NMe_2)_6$ to afford the corresponding monomeric Ga species (NON)$GaNMe_2$ (**2**), in which the four-coordinate Ga center adopts an unusual tmp geometry. Unlike its Al analogues (NON)$AlNMe_2$, species **2** effectively catalyzes the intermolecular hydroamination of terminal akynes by primary amines. Thus, while discrete Ga derivatives are typically less reactive than their Al analogues for the mediation of numerous organic reactions (such as various Lewis acid assisted reactions), the present results further illustrate that Ga derivatives may be a profitable alternative (in catalysis) where Al analogues fail.

Further studies in this area will focus on the characterization of key intermediates relevant to these hydroamination reactions and on widening the scope of application of this catalysis.

EXPERIMENTAL SECTION

All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene and pentane were collected after being passed through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. C_6D_6 was purchased from Eurisotop (CEA, Saclay, France), distilled from CaH_2, degassed under a N_2 flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. All other chemicals were purchased from Aldrich and were used as received, with the exception of the amines and the alkynes: the latter were all distilled over KOH and subsequently stored over activated molecular sieves (4 Å) for at least 24 h in a glovebox prior to use. The NMR spectra were recorded on Bruker AC 300 and 400 MHz NMR spectrometers in Teflon-valved J. Young NMR tubes at ambient temperature unless indicated otherwise. ^1H and ^{13}C chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Elemental analyses were performed at the Service de Microanalyse of the Université de Strasbourg (Strasbourg, France). The diamino-ether ligand **1** and $Ga_2(NMe_2)_6$ were prepared according to reported literature procedures.[18]

$\{\eta^3$-*N,O,N*-$((C_5H_9)N\text{-}C_6H_4)_2O\}GaNMe_2$ (2). In a nitrogen-filled glovebox, the diamino-ether ligand $(C_5H_9NH\text{-}C_6H_4)_2O$ (**1**; 770 mg, 2.29 mmol) was charged in a Schlenk flask and a toluene solution (10 mL) of $Ga_2(NMe_2)_6$ (460 mg, 1.15 mmol) was added to yield a colorless solution. The reaction mixture was then heated for 40 h at 100 °C in an oil bath to yield a pale yellow solution that was subsequently cooled to room temperature and evaporated to dryness in vacuo, affording an off-white solid residue. The latter was dissolved in pentane and cooled to −35 °C over 5 days. The Ga complex **2** precipitated as a white solid that was further dried under vacuum (525 mg, 51% yield). Anal. Calcd for $C_{25}H_{33}GaN_2O$: C, 64.31; H, 7.20; N, 9.37. Found: C, 63.29; H, 6.99; N, 9.25. ^1H NMR (400 MHz, C_6D_6): δ 7.26 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz, 2H), 7.05 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 6.68 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz, 2H), 6.42 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, 2H), 3.81 (q, $^3J_{HH}$ = 7.5 Hz, 2H), 2.73 (s, 6H), 1.42−2.27 (m, 16H). ^{13}C NMR (400 MHz, C_6D_6): δ 146.5 (C_{ipso}), 145.5 (C_{ipso}), 127.4 (Ar), 119.1 (Ar), 113.6 (Ar), 113.0 (Ar), 57.7 (CH-C_5H_9), 41.6 (Ga-NMe_2), 34.9 (C_5H_9), 34.7 (C_5H_9), 24.9 (C_5H_9), 24.7 (C_5H_9).

$[\{\eta^2$-*N,N*-$((C_5H_9)N\text{-}C_6H_4)_2O\}Ga(\mu\text{-}NHPh)]_2$ (3). In a nitrogen-filled glovebox, the Ga-NMe_2 complex **2** (180 mg, 0.40 mmol) was charged in a Schlenk flask and a toluene solution (10 mL) of aniline (37.8 mg, 0.40 mmol) was added to yield a colorless solution. The reaction mixture was then heated overnight at 100 °C in an oil bath to yield a pale yellow solution that was subsequently cooled to room temperature and evaporated to dryness in vacuo, affording an off-white solid residue. The latter was dissolved in dichloromethane and cooled to −35 °C overnight. The Ga complex **3** crystallized as a colorless solid that was further dried under vacuum (40 mg, 20% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.26 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 4H), 7.05 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 4H), 6.71 (m, 10H), 6.68 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 4H), 6.43 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 4H), 3.75 (q, $^3J_{HH}$ = 7.2 Hz, 4H), 3.40 (s, NH, 2H), 1.20−2.10 (m, 32H). ^{13}C NMR (300 MHz, C_6D_6): δ 150.4 (C_{ipso}), 147.0 (C_{ipso}), 145.0 (C_{ipso}) 129.6 (Ar), 128.3 (Ar), 127.7 (Ar), 119.2 (Ar), 117.4 (Ar), 113.9 (Ar), 113.2 (Ar), 57.5 (CH-C_5H_9), 35.3 (C_5H_9), 34.9 (C_5H_9), 24.6 (C_5H_9), 24.5 (C_5H_9).

General Procedure for the Hydroamination Catalysis. In a nitrogen-filled glovebox, the appropriate amounts of alkyne and amine were added by syringe and dissolved in C_6D_6 in a vial equipped with a Teflon-tight screw cap. The Ga complex **2** as well as an internal standard (C_6Me_6, 0.2 equiv vs substrates) were then added to yield a colorless solution. The vial was tightly closed, placed in a temperature-controlled oil bath (100 °C), and heated for the appropriate time. The mixture was subsequently cooled to room temperature and hydrolyzed with aqueous HCl (1 M). Conversion of the reagents was monitored by ^1H NMR spectroscopy of the C_6D_6 organic phase: i.e., the ratios between the alkyne substrate and the hydrolysis products (i.e. the corresponding ketones) were calculated from the integral intensities of the corresponding signals. In all cases, the reagents either did not react or were converted to the expected hydroamination products, as deduced from the ^1H NMR integration ratio (reagents + hydroamination product)/internal standard.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving a summary of X-ray crystallographic data for complexes **2** and **3** and graphs associated with kinetic studies on compound **2** mediated hydroamination of 1-hexene by aniline. This material is available free of charge via the Internet at http://pubs.acs.org.

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