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View Article Online
View Journal | View IssueCite this: *Dalton Trans.*, 2017, **46**,
1406Received 5th December 2016,
Accepted 30th December 2016

DOI: 10.1039/c6dt04595b

rsc.li/dalton

Azido- and amido-substituted gallium hydrides
supported by N-heterocyclic carbenes†

Anindya K. Swarnakar, Michael J. Ferguson, Robert McDonald and Eric Rivard*

Despite recent advances in main group N-heterocyclic carbene (NHC) coordination chemistry, gallium hydrides remain, in large part, an unexplored area of research. In this paper we outline efficient routes to azido- and amido-functionalized gallium hydrides such as $\text{NHC}\cdot\text{GaH}_2\text{N}_3$ and $\text{NHC}\cdot\text{GaH}_2\text{N}(\text{SiMe}_3)_2$ and explore these species as potential precursors to HGaNH complexes and bulk gallium nitride (GaN).

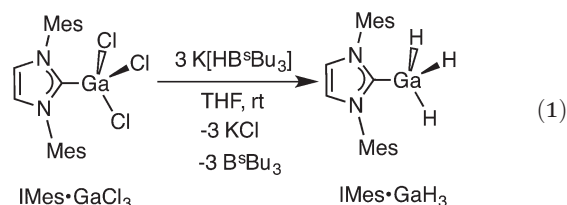
Introduction

It is now well accepted that the coordination of main group element centers by carbon-based donors, such as N-heterocyclic carbenes (NHCs),¹ cyclic(alkyl)aminocarbenes (CAACs),² and N-heterocyclic olefins (NHOs)³ can provide access to many species that are unstable or unattainable under conventional synthetic conditions. Drawing focus to the Group 13 (triel) elements, the recent isolation of homodiatom B_2 molecular adducts⁴ can be viewed as a particularly salient example of the stabilization brought forth by the above-mentioned carbon-based donors.

Recently, our group prepared a complex containing the elusive inorganic acetylene HBNH placed between a sterically encumbered NHC donor and a large triarylfluoroborane acceptor.⁵ The resulting complex $\text{IPr}\cdot\text{HB}=\text{NH}\cdot\text{BAR}^{\text{F}}_3$ [$\text{IPr} = [(\text{HCNDipp})_2\text{C}]$; $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$; $\text{Ar}^{\text{F}} = 3,5\text{-}(\text{F}_3\text{C})_2\text{C}_6\text{H}_3$] was synthesized *via* Lewis acid-assisted N_2 elimination from the non-explosive azidoborane complex $\text{IPr}\cdot\text{BH}_2\text{N}_3$ ⁶ followed by hydride migration from B to N. This prompted us to explore parallel chemistry⁷ with gallium, wherein the iminogallane $\text{HGa}=\text{NH}$ could be a possible building block for the future low temperature deposition of bulk gallium nitride (GaN), a highly valued material for its luminescent and semi-conducting properties.^{8,9} Our preliminary investigations involving the preparation of NHC-supported azido- and amido-gallium hydrides and behavior upon heating are reported herein.

Results and discussion

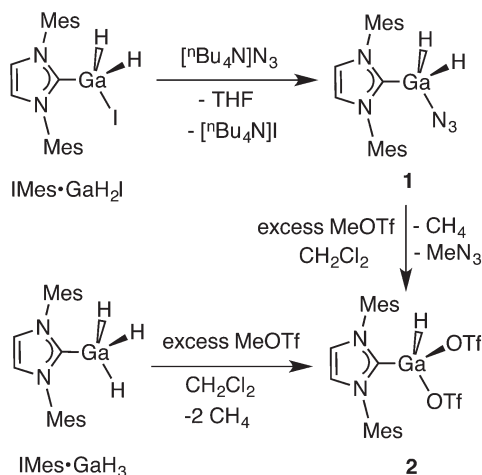
Our attempted synthesis of an $\text{HGa}=\text{NH}$ complex required the discovery of a suitable route to an azidogallane adduct $\text{NHC}\cdot\text{GaH}_2\text{N}_3$. We hoped that one analogue, $\text{IMes}\cdot\text{GaH}_2\text{N}_3$, could be synthesized from known $\text{IMes}\cdot\text{GaH}_2\text{X}$ ($\text{IMes} = [\{\text{HCN}(\text{Mes})\}_2\text{C}]$; $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$; $\text{X} = \text{Cl}, \text{Br}$ or I) complexes¹⁰ by reaction with common azide sources such as Me_3SiN_3 or NaN_3 . However previous reports associated with the synthesis of the necessary starting material $\text{IMes}\cdot\text{GaH}_3$ involved the reaction of the N-heterocyclic carbene, IMes , with thermally unstable $\text{Li}[\text{GaH}_4]$.¹¹ To make an eventual route to $\text{IMes}\cdot\text{GaH}_2\text{N}_3$ more convenient, we developed a modified synthesis of $\text{IMes}\cdot\text{GaH}_3$ using $\text{K}[\text{HB}^{\text{s}}\text{Bu}_3]$ as a hydride source. Specifically $\text{IMes}\cdot\text{GaCl}_3$ ¹² was combined with three equivalents of $\text{K}[\text{HB}^{\text{s}}\text{Bu}_3]$ in THF at room temperature to give $\text{IMes}\cdot\text{GaH}_3$ in a 75% isolated yield *via* Cl/H exchange (eqn (1)). Later, $\text{IMes}\cdot\text{GaH}_3$ was treated with 0.5 equivalents of $\text{IMes}\cdot\text{GaI}_3$, according to literature procedures,^{10c,12} to afford $\text{IMes}\cdot\text{GaH}_2\text{I}$.



In order to synthesize the desired azido-gallane adduct $\text{IMes}\cdot\text{GaH}_2\text{N}_3$, $\text{IMes}\cdot\text{GaH}_2\text{I}$ was reacted with either Me_3SiN_3 or NaN_3 in THF; however, no reaction transpired. A successful synthesis of $\text{IMes}\cdot\text{GaH}_2\text{N}_3$ (**1**) was accomplished by combining $\text{IMes}\cdot\text{GaH}_2\text{I}$ with the lipophilic azide salt $[\text{Bu}_4\text{N}]\text{N}_3$ in THF (Scheme 1). The ^1H NMR spectrum of the resulting product (**1**) afforded a broad resonance at 4.52 ppm, due to the retention of two gallium-bound hydrides. Moreover, a diagnostic azide

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive,
Edmonton, Alberta, Canada T6G 2G2. E-mail: erivard@ualberta.ca

†Electronic supplementary information (ESI) available: Tables of crystallographic data for compounds 1–5. CCDC 1519736–1519740. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt04595b



Scheme 1 Synthesis of IMes-GaH₂N₃ (1) and its conversion into IMes-GaH(OTf)₂ (2).

$\tilde{\nu}(\text{N}_3)$ band for compound 1 was detected at 2084 cm⁻¹, which matched well with the related asymmetric azide stretch at 2104 cm⁻¹ found in Me₃N-GaCl₂N₃.^{9b} The composition of 1 was substantiated by X-ray crystallography (Fig. 1) and revealed

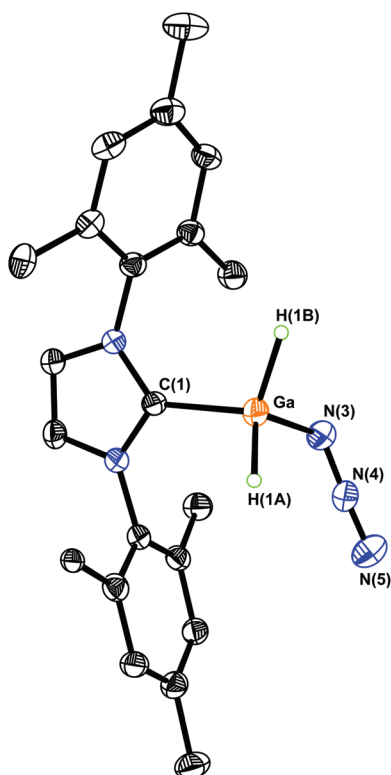
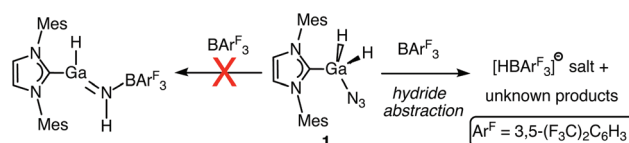


Fig. 1 Molecular structure of IMes-GaH₂N₃ (1) with thermal ellipsoids presented at a 30% probability level; all carbon bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–C(1) 2.041(4), Ga–N(3) 1.953(4), Ga–H(1A) 1.52(5), Ga–H(1B) 1.52(5), N(3)–N(4) 1.199(6), N(4)–N(5) 1.146(6); N(3)–Ga–C(1) 101.41(18), N(3)–N(4)–N(5) 174.6(6).

the presence of a tetrahedral geometry about the Ga center. The C_(NHC)–Ga bond distance in 1 is 2.041(4) Å and is similar to values found within known NHC-gallane complexes.^{10,12} The Ga–N bond length in 1 is 1.953(4) Å and comparable to the Ga–N bond distances in Christie's pentaazido gallate salt [PPh₄]₂[Ga(N₃)₅] [1.937(2)–2.049(2) Å].¹³

After the successful isolation of IMes-GaH₂N₃ (1), we explored the possible Lewis acid-triggered N₂ elimination/hydride migration from Ga to N to form IMes-HGa=NH-BAr₃^F (Ar^F = 3,5-(F₃C)₂C₆H₃); a similar transformation was previously used to yield an HB=NH complex.⁵ Accordingly, IMes-GaH₂N₃ was combined with a stoichiometric amount of BAr₃^F followed by the heating of the reaction mixture to 80 °C in toluene. The ¹H NMR spectrum of the resulting white solid indicated the formation of multiple carbene-containing products, however conclusive evidence for the formation of an HGa=NH complex was not found. Instead, a salt consisting of the known [HBar₃^F][−] anion¹⁴ was identified (Scheme 2) as one of the products in the mixture by ¹H and ¹¹B NMR spectroscopy. Attempts to isolate pure products by fractional crystallization were unsuccessful.

It was previously reported that N₂ loss/1,2-hydride migration in IPr-BH₂N₃ could also be instigated by addition of the strong electrophile MeOTf (OTf = OSO₂CF₃), leading to the formation of the *N*-methylated adduct [IPr-HB=NHMe]OTf.^{5a} However when IMes-GaH₂N₃ (1) was treated with one equivalent of MeOTf in CH₂Cl₂, multiple products were found according to ¹H and ¹⁹F NMR spectroscopy. Increasing the stoichiometry of MeOTf to four molar equivalents resulted in clean formation of the new hydrido/triflate adduct IMes-GaH(OTf)₂ (2) (Scheme 1) in a 80% yield as a colorless moisture-sensitive solid. Compound 2 was identified by a combination of X-ray crystallography (Fig. 2) and NMR spectroscopy. Due to the possible explosive nature of the likely by-product, MeN₃ (**Caution!**),¹⁵ this reaction was not repeated again. However the outcome of the reaction was further confirmed by an independent synthesis of 2 by combining IMes-GaH₃ with excess MeOTf (Scheme 1). The ¹⁹F NMR spectrum of IMes-GaH(OTf)₂ (2) afforded a sharp resonance at −77.4 ppm that was assigned to covalently bound OTf groups. As shown in Fig. 2, the refined structure of 2 afforded the expected coordination of two OTf[−] substituents at gallium with corresponding Ga–O bond lengths of 1.9023(15) and 1.9186(16) Å. These bonds are significantly elongated relative to those [1.8021(1) Å] in the four-coordinate bis(hydroxy)gallium complex LGa(OH)₂ (L = HC[C(Me)NDipp]₂; Dipp = 2,6-ⁱPr₂C₆H₃),¹⁶ suggesting that the Ga-OTf interactions in 2 are weak in nature.



Scheme 2 Reaction of IMes-GaH₂N₃ (1) with BAr₃^F.



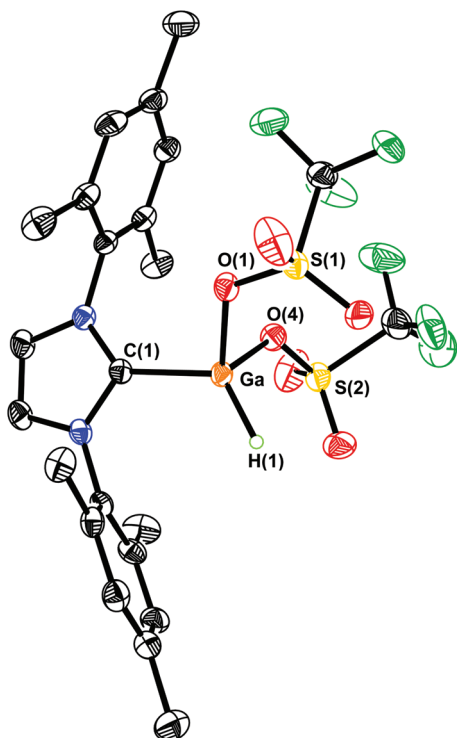


Fig. 2 Molecular structure of IMes-GaH(OTf)₂ (**2**) with thermal ellipsoids presented at a 30% probability level; all carbon bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–C(1) 1.9855(19), Ga–O(1) 1.9023(15), Ga–O(4) 1.9186(16), Ga–H(1) 1.45(3); O(1)–Ga–C(1) 104.12(7), C(1)–Ga–H(1) 123.2(11).

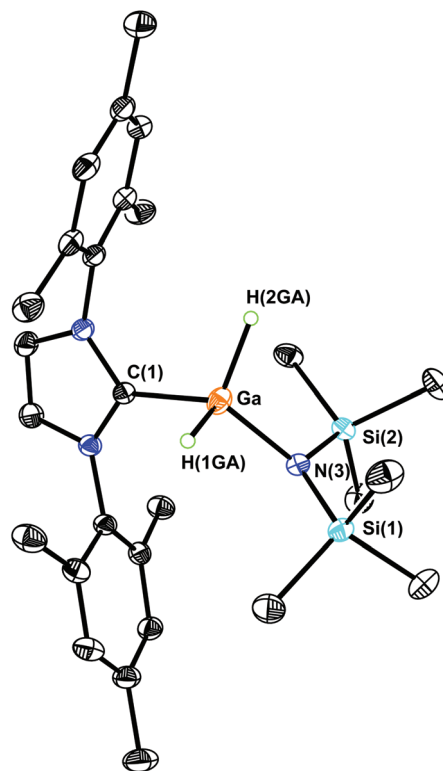
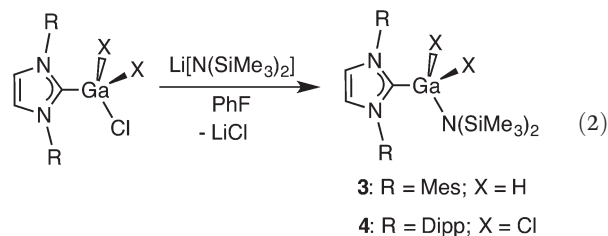


Fig. 3 Molecular structure of IMes-GaH₂N(SiMe₃)₂ (**3**) with thermal ellipsoids presented at a 30% probability level; all carbon bound hydrogen atoms have been omitted for clarity; **3** co-crystallizes with ca. 15% of the mixed hydrido/chloride adduct IMes-GaH(Cl)–N(SiMe₃)₂. Selected bond lengths (Å) and angles (°) for **3**: Ga–C(1) 2.0743(15), Ga–H(1GA) 1.503(18), Ga–H(2GA) 1.512(19), Ga–N(3) 1.9226(13); N(3)–Ga–C(1) 112.30(6), Si(1)–N(3)–Si(2) 123.25(8), Ga–N(3)–Si(1) 112.09(7), Ga–N(3)–Si(2) 118.07(7).

The above results indicate that in the presence of a Lewis acid (BAR^F₃) or electrophile MeOTf, IMes-GaH₂N₃ (**1**) undergoes preferential azide or hydride abstraction processes in place of N₂ loss/hydride migration. The differing reactivity of the azido-gallane IMes-GaH₂N₃ (**1**) compared with IPr-BH₂N₃ is likely a consequence of the increased polarity and reactivity of Ga–N and Ga–H bonds due to the lower electronegativity of Ga in relation to B. Thus it appears that an alternate route to a molecular complex of HGa=NH has to be devised.

In keeping with the theme of eventually generating molecular precursors to bulk gallium nitride, we prepared the gallium-silylamide complexes IMes-GaH₂N(SiMe₃)₂ (**3**) and IPr-GaCl₂N(SiMe₃)₂ (**4**). The amido-gallane complex IMes-GaH₂N(SiMe₃)₂ (**3**) was prepared in a 93% yield as a white solid from the reaction of IMes-GaH₂Cl¹² with a stoichiometric amount of Li[N(SiMe₃)₂] (eqn (2)). The ¹H NMR spectrum of **3** afforded a sharp up-field positioned resonance at 0.23 ppm due to the capping –N(SiMe₃)₂ group, while expected resonances for the gallium hydrides (4.51 ppm) and IMes ligand were also found. The crystallographically determined structure of **3** is found in Fig. 3; despite the presence of co-crystallized IMes-GaH(Cl)–N(SiMe₃)₂ as part of the crystalline lattice, bulk samples of **3** afforded both satisfactory elemental analyses and clean NMR spectra. Perhaps the most salient structural feature of **3** is the substantially longer

C_(NHC)–Ga length [2.0743(15) Å] in relation to that found in the bis(triflate)gallane IMes-GaH(OTf)₂ (**2**) [1.9855(19) Å]; this is likely a consequence of the less Lewis acidic GaH₂N(SiMe₃)₂ unit in **3** in relation to the GaH(OTf)₂ moiety in **2**. The nitrogen atom within the silylamido group in **3** [N(3); Fig. 3] is slightly pyramidalized as revealed by an angle sum (Σ°N) value of 353.41(12)°. Due to the presence of the bulky SiMe₃ groups at nitrogen, the Ga–N bond distance in **3** [1.9226(13) Å] is longer compared to the Ga–NMe₂ bond length [1.816(2) Å] reported in {[cyclopentyl]N–C₆H₄]₂O}GaNMe₂.¹⁷



A halogenated analogue of **3**, IPr-GaCl₂N(SiMe₃)₂ (**4**) was also readily prepared from the known adduct IPr-GaCl₃^{12b} and one equivalent of Li[N(SiMe₃)₂] (eqn (2)). The molecular



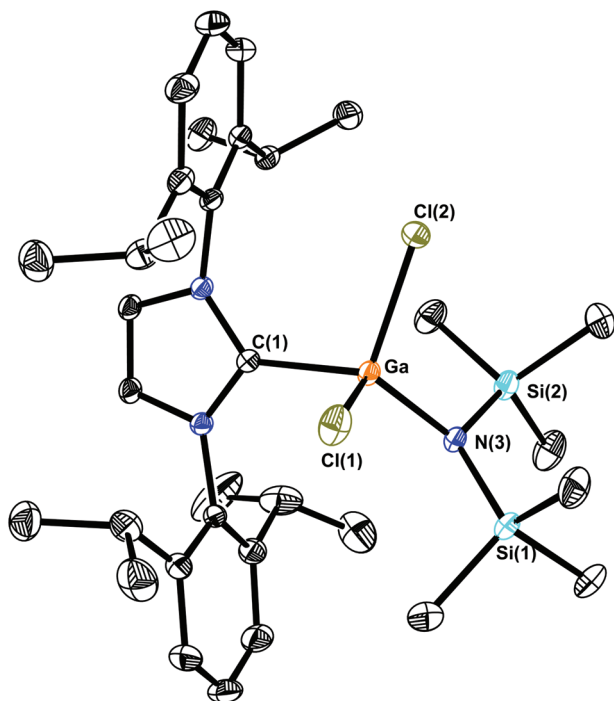


Fig. 4 Molecular structure of $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_2)_2$ (4) with thermal ellipsoids presented at a 30% probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–C(1) 2.0570(15), Ga–N(3) 1.8932(13), Ga–Cl(1) 2.2054(4), Ga–Cl(2) 2.2047(5); N(3)–Ga–C(1) 119.05(6), Cl(1)–Ga–Cl(2) 103.54(2), Si(2)–N(3)–Si(1) 121.46(8).

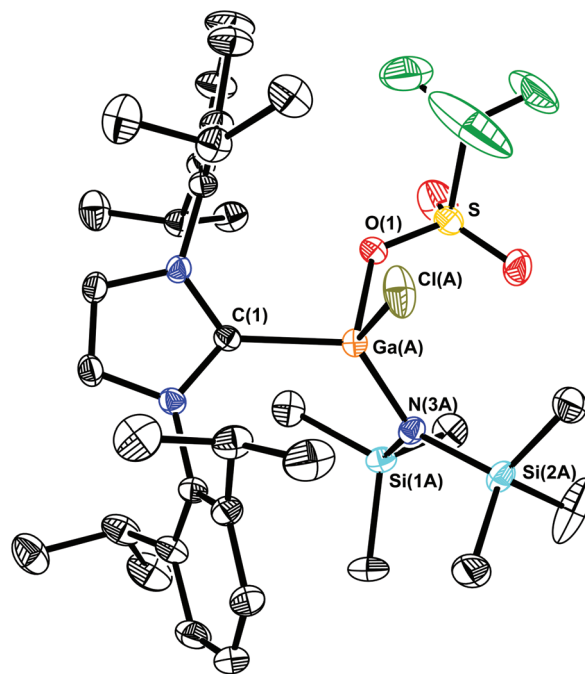


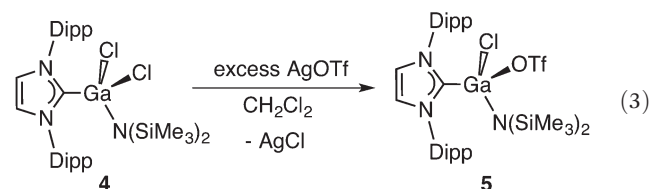
Fig. 5 Molecular structure of $\text{IPr-GaCl}(\text{OTf})\text{N}(\text{SiMe}_2)_2$ (5) with thermal ellipsoids presented at a 30% probability level; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with parameters associated with a second molecule in the asymmetric unit listed in square brackets: Ga(A)–C(1) 2.042(3) [2.167(6)], Ga(A)–N(3A) 1.846(3) [1.840(9)], Ga(A)–Cl(A) 2.1668(11) [2.171(10)], Ga(A)–O(1) 1.969(2) [1.982(5)]; N(3A)–Ga(A)–C(1) 124.52(14) [129.1(11)], Cl(A)–Ga(A)–O(1) 102.10(9) [112.5(15)].

structure of $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ is found in Fig. 4 and displays similar overall structural features as the hydrido congener 3.

After the successful preparation of $\text{IMes-GaH}_2\text{N}(\text{SiMe}_3)_2$ (3) and $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ (4), we decided to explore the possible formation of extended GaN structures⁹ *via* thermolysis. To our surprise, both of these species are quite thermally stable and do not show any signs of HSiMe_3 , ClSiMe_3 or $\text{HN}(\text{SiMe}_3)_2$ loss upon heating to 100 °C in toluene. Compound 3 was also stable upon microwave irradiation for 1.5 h at 130 °C in toluene, while under the same microwave conditions, compound 4 underwent partial decomposition to an $[\text{IPrH}]^+$ salt (20%) and a new unidentified carbene-containing product (24%).

We then decided to promote possible intermolecular Ga–N bond forming processes by replacing the chloride substituents in $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ (4) with more labile OTf^- groups (to form $\text{IPr-Ga}(\text{OTf})_2\text{N}(\text{SiMe}_3)_2$). Towards this goal, $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ (4) was combined with two equiv. of $\text{Ag}[\text{OTf}]$ in CH_2Cl_2 , however under these conditions the replacement of only one chloride transpired to form $\text{IPr-GaCl}(\text{OTf})\text{N}(\text{SiMe}_3)_2$ (5). Compound 5 was obtained as a racemic mixture due to the presence of a chiral gallium center (eqn (3); Fig. 5). A sharp signal at -76.2 ppm in the ^{19}F NMR spectrum of 5 indicated that the OTf group remained covalently bound to gallium in solution. Despite replacing one of the chlorine atoms with a

OTf group, compound 5 was also thermally stable to 100 °C in toluene for 12 h. However, compound 5 underwent complete decomposition to several unidentified products upon microwave irradiation for 1.5 h at 130 °C in fluorobenzene.



Conclusions

In this article, the successful isolation of N-heterocyclic carbene complexes of azido- and amido-gallanes has been described. These species represent members of a general compound class that could be eventually used to generate bulk gallium nitride under mild conditions (after suitable ligand modification). The reported gallium hydrides also have similar structural features as our recently reported active ketone hydrosilylation/borylation catalyst $\text{IPr-Zn}(\text{H})\text{OTf}\cdot\text{THF}$ ^{18a} and thus we are now exploring the catalytic activity¹⁸ of these main group, NHC-supported, gallium hydrides in more detail.



Experimental

Materials and instrumentation

All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology, Inc.).¹⁹ Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technology, Inc., degassed (freeze-pump-thaw method), and stored under an atmosphere of nitrogen prior to use. $\text{K}[\text{HB}^s\text{Bu}_3]$ (1.0 M solution in THF), GaCl_3 , $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, and $[\text{tBu}_4\text{N}]\text{N}_3$ were purchased from Aldrich and used as received. NHC-GaX_3 ($\text{NHC} = \text{IMes}$ or IPr ; $\text{X} = \text{Cl}$ or I),^{12b,20} $\text{IMes-GaH}_2\text{X}$ ($\text{X} = \text{Cl}$ or I)^{10a,c} and BAR^{F}_3 ($\text{Ar}^{\text{F}} = 3,5\text{-(F}_3\text{C)}_2\text{C}_6\text{H}_3$)²¹ were prepared according to literature procedures. ^1H , ^{11}B , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to SiMe_4 (^1H and $^{13}\text{C}\{^1\text{H}\}$), $\text{F}_3\text{B-OEt}_2$ (^{11}B), and CFCl_3 (^{19}F) respectively. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp apparatus and are uncorrected.

X-ray crystallography

Crystals of suitable quality for X-ray diffraction studies were removed from a vial in a glovebox and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on an X-ray diffractometer.²² All data were collected at the University of Alberta using a Bruker APEX II CCD detector/D8 diffractometer using $\text{Cu K}\alpha$ radiation with the crystals cooled to -100°C . The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces.²³ Structures were solved using the direct methods program SHELXS-97²⁴ ($\text{IPr-GaCl}(\text{OTf})\text{N}(\text{SiMe}_3)_2$ (5)) or intrinsic phasing SHELXT²⁴ ($\text{IMes-GaH}_2\text{N}_3$ (1), $\text{IMes-GaH}(\text{OTf})_2$ (2), $\text{IMes-GaH}_2\text{N}(\text{SiMe}_3)_2$ (3), $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ (4)). Structure refinement was accomplished using either SHELXL-97 or SHELXL-2013.²⁴ All carbon-bound hydrogen atoms were assigned positions on the basis of the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Synthetic procedures

Synthesis of IMes-GaH_3 . To a 40 mL THF solution of IMes-GaCl_3 (1.67 g, 3.48 mmol) was added dropwise $\text{K}[\text{HB}^s\text{Bu}_3]$ (11 mL, 1.0 M solution in THF, 11 mmol) and the mixture was stirred for 24 h. The mother liquor was separated from the white precipitate by filtration and the solvent was removed under vacuum from the filtrate. The resulting product was washed three times with hexanes (3×10 mL) and dried under vacuum to yield IMes-GaH_3 as a white powder (980 mg, 75%). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra matched those found in the literature.^{10a}

Synthesis of $\text{IMes-GaH}_2\text{N}_3$ (1). To a 3 mL THF solution of $\text{IMes-GaH}_2\text{I}$ (154 mg, 0.31 mmol), was added dropwise a 3 mL THF solution of $[\text{tBu}_4\text{N}]\text{N}_3$ (77 mg, 0.28 mmol) and the reaction mixture was stirred for 3 h. The solvent was removed from the mixture under vacuum and the resulting white solid was re-dissolved in 20 mL of toluene. The solution was filtered and the solvent was removed from the filtrate under vacuum to yield $\text{IMes-GaH}_2\text{N}_3$ (1) (80 mg, 62%) as a white solid. Crystals suitable for X-ray diffraction were grown from a mixture of toluene/hexanes mixture at -35°C . ^1H NMR (400 MHz, C_6D_6): $\delta = 6.74$ (s, 4H, ArH), 5.96 (s, 2H, ArH), 4.52 (br, 2H, GaH), 2.07 (s, 6H, CH_3), 1.98 (s, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): $\delta = 171.7$ (s, N-C-N), 140.1 (s, ArC), 134.9 (s, ArC), 134.2 (s, ArC), 129.6 (s, ArC), 123.0 (s, N-CH), 21.1 (s, CH_3), 17.4 (s, CH_3). IR (Nujol, cm^{-1}): 2084 (s, $\tilde{\nu}_{\text{N}_3}$), 1890 (m, $^{\text{asym}}\tilde{\nu}_{\text{Ga-H}}$), 1843 (m, $^{\text{sym}}\tilde{\nu}_{\text{Ga-H}}$). Anal. calcd for $\text{C}_{21}\text{H}_{26}\text{GaN}_3$: C, 60.31; H, 6.21; N, 16.75. Found: C, 60.13; H, 6.22; N, 16.55%. Mp ($^\circ\text{C}$): 183–186.

Independent synthesis of $\text{IMes-GaH}(\text{OTf})_2$ (2). To a 5 mL CH_2Cl_2 solution of IMes-GaH_3 (96 mg, 0.25 mmol) was added MeOTf (114 μL , 1.04 mmol) and the mixture was stirred for 12 h. All the volatiles were removed under vacuum and the resulting white solid was washed with 5 mL of hexanes. The product was dried under vacuum to yield 2 as a white powder (140 mg, 83%). ^1H NMR (400 MHz, C_6D_6): $\delta = 6.72$ (s, 4H, ArH), 5.89 (s, 2H, N-CH), 5.10 (br, 1H, GaH), 2.02 (s, 6H, CH_3), 1.94 (s, 12H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): $\delta = 158.0$ (s, N-C-N), 141.8 (s, ArC), 134.7 (s, ArC), 131.7 (s, ArC), 130.1 (s, ArC), 125.1 (s, N-CH), 119.9 (q, $^1J_{\text{CF}} = 318$ Hz, CF_3), 21.0 (s, CH_3), 17.1 (s, CH_3). ^{19}F NMR (376 MHz, C_6D_6): $\delta = -77.4$. IR (Nujol, cm^{-1}): 2062 (m, $\tilde{\nu}_{\text{Ga-H}}$). Anal. calcd for $\text{C}_{23}\text{H}_{25}\text{F}_6\text{GaN}_2\text{O}_6\text{S}_2$: C, 41.03; H, 3.74; N, 4.16; S, 9.52. Found: C, 40.23; H, 3.67; N, 4.01; S, 9.52%. Mp ($^\circ\text{C}$): 180–185.

Synthesis of $\text{IMes-GaH}_2\text{N}(\text{SiMe}_3)_2$ (3). To a 5 mL fluorobenzene solution of $\text{IMes-GaH}_2\text{Cl}$ (159 mg, 0.39 mmol), was added a 5 mL fluorobenzene solution of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (65 mg, 0.39 mmol) and the mixture was stirred for 12 h. The volatiles were then removed under vacuum and the resulting white solid was re-dissolved in 20 mL of Et_2O and filtered. The solvent was removed under vacuum from the filtrate to yield 3 as a white powder (190 mg, 93%). Crystals suitable for X-ray diffraction were grown from toluene/hexanes at -35°C . ^1H NMR (400 MHz, C_6D_6): $\delta = 6.77$ (s, 4H, ArH), 5.96 (s, 2H, N-CH), 4.51 (br, 2H, GaH), 2.10 (s, 6H, CH_3), 2.07 (s, 12H, CH_3), 0.23 (s, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): $\delta = 176.8$ (s, N-C-N), 139.6 (s, ArC), 135.1 (s, ArC), 129.8 (s, ArC), 128.6 (s, ArC), 122.9 (s, N-CH), 21.0 (s, CH_3), 18.3 (s, CH_3), 5.5 (s, $\text{Si}(\text{CH}_3)_3$). IR (Nujol, cm^{-1}): 1833 (s, $^{\text{asym}}\tilde{\nu}_{\text{Ga-H}}$), 1805 (s, $^{\text{sym}}\tilde{\nu}_{\text{Ga-H}}$). Anal. calcd for $\text{C}_{27}\text{H}_{44}\text{GaN}_3\text{Si}_2$: C, 60.44; H, 8.27; N, 7.83. Found: C, 60.29; H, 7.96; N, 7.42%. Mp ($^\circ\text{C}$): 150–155.

Synthesis of $\text{IPr-GaCl}_2\text{N}(\text{SiMe}_3)_2$ (4). A 5 mL fluorobenzene solution of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (29 mg, 0.17 mmol) was dropwise added to a 10 mL fluorobenzene solution of IPr-GaCl_3 (105 mg, 0.19 mmol). The resulting white slurry was stirred for 12 h and all the volatiles were removed under vacuum. The remaining white powder was dissolved in 20 mL of Et_2O and filtered. The solvent was removed under vacuum from the



filtrate to yield **4** as a white solid (95 mg, 74%). Crystals suitable for X-ray diffraction were grown from Et₂O/hexanes at −35 °C. ¹H NMR (400 MHz, C₆D₆): δ = 7.24 (t, ³J_{H-H} = 8.0 Hz, 2H, ArH), 7.13 (d, ³J_{H-H} = 7.5 Hz, 4H, ArH), 6.40 (s, 2H, N-CH-), 2.92 (sept, ³J_{H-H} = 6.5 Hz, 4H, CH(CH₃)₂), 1.48 (d, ³J_{H-H} = 7.0 Hz, 12H, CH(CH₃)₂), 0.91 (d, ³J_{H-H} = 7.0 Hz, 12H, CH(CH₃)₂), 0.30 (s, 18H, Si(CH₃)₃). ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 167.0 (s, N-C-N), 145.9 (s, N-CH), 134.9 (s, ArC), 131.5 (s, ArC), 126.0 (s, ArC), 124.7 (s, ArC), 29.1 (s, CH(CH₃)₂), 26.4 (s, CH(CH₃)₂), 23.1 (s, CH(CH₃)₂), 6.5 (s, Si(CH₃)₃). Anal. calcd for C₃₃H₅₄Cl₂GaN₃Si₂: C, 57.48; H, 7.89; N, 6.09. Found: C, 57.96; H, 7.88; N, 5.78%. Mp (°C): 165–170.

Synthesis of IPr-GaCl(OTf)N(SiMe₃)₂ (5**).** A solution of IPr-GaCl₂N(SiMe₃)₂ (**4**) (150 mg, 0.22 mmol) in 10 mL of CH₂Cl₂ was added to a 5 mL CH₂Cl₂ solution of AgOTf (123 mg, 0.47 mmol) and the mixture was stirred for 2 h. The resulting slurry was filtered and the volatiles were removed from the filtrate to yield **5** as an off-white powder (130 mg, 74%). Crystals suitable for X-ray diffraction were grown from fluorobenzene/hexanes at −35 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.54 (t, ³J_{H-H} = 7.7 Hz, 2H, ArH), 7.39–7.35 (m, 4H, ArH), 7.20 (s, 2H, N-CH-), 2.82 (sept, ³J_{H-H} = 6.5 Hz, 2H, CH(CH₃)₂), 2.73 (sept, ³J_{H-H} = 6.5 Hz, 2H, CH(CH₃)₂), 1.46 (d, ³J_{H-H} = 6.5 Hz, 6H, CH(CH₃)₂), 1.42 (d, ³J_{H-H} = 6.5 Hz, 6H, CH(CH₃)₂), 1.08 (d, ³J_{H-H} = 7.5 Hz, 6H, CH(CH₃)₂), 1.07 (d, ³J_{H-H} = 7.5 Hz, 6H, CH(CH₃)₂), 0.07 (br, 9H, Si(CH₃)₃), −0.15 (br, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 163.2 (s, N-C-N), 145.5 (s, N-CH), 145.3 (s, N-CH), 133.9 (s, ArC), 131.8 (s, ArC), 127.0 (s, ArC), 125.2 (s, ArC), 125.0 (s, ArC), 118.7 (q, ¹J_{CF} = 319.6 Hz, CF₃), 29.1 (s, CH(CH₃)₂), 29.0 (s, CH(CH₃)₂), 27.0 (s, CH(CH₃)₂), 26.8 (s, CH(CH₃)₂), 22.7 (s, CH(CH₃)₂), 22.5 (s, CH(CH₃)₂), 5.8 (br, Si(CH₃)₃), 5.4 (br, Si(CH₃)₃). ¹⁹F NMR (376 MHz, CDCl₃): δ = −76.2 (s, CF₃). Anal. calcd for C₃₄H₅₄ClF₃GaN₃O₃SSi₂: C, 50.84; H, 6.78; N, 5.23. Found: C, 50.17; H, 6.56; N, 5.07%. Mp (°C): 177–182.

Reaction of **1 with MeOTf.** To a 10 mL CH₂Cl₂ solution of IMes-GaH₂N₃ (**1**) (156 mg, 0.37 mmol) was added MeOTf (163 μL, 1.48 mmol) and the mixture was stirred for 12 h. All the volatiles were removed under vacuum and the resulting white solid was washed with 10 mL of hexanes. The product was dried under vacuum to yield **2** as a white powder (202 mg, 80%). Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/hexanes at −35 °C. ¹H, ¹³C{¹H} and ¹⁹F NMR spectra: same as compound **2** (see above).

Reaction of **1 with BAR^F₃.** A solution of BAR^F₃ (171 mg, 0.26 mmol) in 10 mL CH₂Cl₂ was added dropwise to a 5 mL CH₂Cl₂ solution of IMes-GaH₂N₃ (**1**) (110 mg, 0.26 mmol). The mixture was stirred for 2 h and the volatiles were removed under vacuum. The product was then dissolved in 10 mL of toluene and heated to 80 °C for 12 h to give a colorless solution. All the volatiles were removed under vacuum and washed with 10 mL of hexanes and dried. The resulting white solid represented the formation of several products. Attempts to fully characterize the products were unsuccessful, however a salt consisting of the [HBAR^F₃][−] anion was identified as one of the products by ¹H and ¹¹B NMR spectroscopy.¹⁴

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (Discovery Grant and CREATE grants for E. R.; CREATE fellowship for A. K. S.), and the Canada Foundation for Innovation (CFI).

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