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Convenient Access to Gallium(I) Cations through Hydrogen Elimination from Cationic Gallium(III) Hydrides

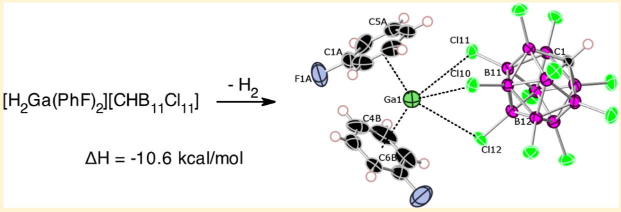
Rudolf J. Wehmschulte,*,† Roberto Peverati,† and Douglas R. Powell‡

†Chemistry Program, Florida Institute of Technology, 150 West University Boulevard, Melbourne, Florida 32901-6975, United States

‡Department of Chemistry and Biochemistry, University of Oklahoma, 101 Stephenson Parkway, Norman, Oklahoma 73019-5251, United States

Supporting Information

ABSTRACT: Although gallium hydrides X_nGaH_{3-n} (X = monoanionic substituent) are usually stable compounds, cationic arene-solvated species $[H_2Ga(arene)_2]^+$ spontaneously eliminate dihydrogen at room temperature to afford the arene-solvated gallium(I) compounds $[Ga(PhF)_2][CHB_{11}Cl_{11}]$ (**1**) and $[Ga(Ph_3CH)][B(C_6F_5)_4]$ (**3**). A key requirement appears to be the presence of a weakly coordinating anion. Use of the more basic triflimide anion, $[NTf_2]^-$, reverses the stability, i.e., the gallium(III) hydride H_2GaNTf_2 (**4**) is more stable than the gallium(I) compound $GaNTf_2$ (**5**). The experimental results are supported by DFT calculations. Compounds **1** and **3** can be used as catalysts for the oligomerization of 2,4,4-trimethyl-1-pentene and the hydrosilylation of benzophenone and 1-hexene.



INTRODUCTION

Although the chemistry of gallium is dominated by the +3 oxidation state,[1] the recently developed access to simple gallium(I) cations[2] is beginning to lead to their application as catalysts in synthetic chemistry. For example, $[Ga(arene)_{2\text{ or }3}][Al\{OC(CF_3)_3\}_4]$ catalyzes the polymerization of isobutene,[3,4] the hydroarylation of alkynes, and the transfer hydrogenation of a trisubstituted olefin,[5] and the in situ generated, crown-ether stabilized gallium(I) triflate catalyzes C−C bond formation involving allyl and allenyl boronic esters and acetals, ketals, and aminals.[6] Furthermore, a gallium(I) site in a Ga-exchanged zeolite is believed to be an active site for the catalytic dehydrogenation of light alkanes,[7] but this finding has been challenged by another paper.[8]

The syntheses of the molecular gallium(I) compounds mentioned above involve the oxidation of gallium metal with a mild oxidant, usually a silver salt such as $Ag[Al\{OC(CF_3)_3\}_4]$[2] or AgOTf (OTf = triflate, Tf = CF_3SO_2),[6] but an alternative approach, the use of a benzene radical cation, $[Me_6C_6][Al\{OC(CF_3)_3\}_4]$ as an oxidizer, was recently reported.[9] Green's "GaI", which seems to be a mixture of several subvalent gallium species,[10−12] is prepared by the oxidation of gallium metal with iodine, and the comproportionation reaction of gallium metal and gallium(III) chloride to afford $Ga[GaCl_4]$ may also be viewed as an oxidation of gallium metal with gallium(III) chloride.[13] Here, we present an alternative route to gallium(I) compounds $[Ga(arene)_n][A]$ ($A = [CHB_{11}Cl_{11}]^-$, $[B(C_6F_5)_4]^-$), namely, the reductive elimination of dihydrogen from $[H_2Ga]^+$ species at room temperature. Contrary to transition-metal chemistry,[14] reductive elimination is still rather uncommon in main group chemistry.[15] Examples involving group 13 compounds include the elimination of H_2 upon thermolysis of $(HGaCl_2)_2$ and $(H_2GaCl)_2$ to afford $Ga[GaCl_4]$[16] and $Ga[GaCl_3H]$,[17] respectively, and the elimination of Cp*H (Cp* = $[Me_5C_5]^-$) from $Cp^*{}_2AlH$ as an alternative approach to $(Cp^*Al)_4$.[18]

The experimental data are supported by quantum-chemical calculations, and results of an exploratory survey of the catalytic activities of the new compounds in the hydrosilylation of 1-hexene, benzophenone, and CO_2 and the oligomerization of 2,4,4-trimethyl-1-pentene are also included.

RESULTS AND DISCUSSION

The first crystals of the gallium(I) species $[Ga(C_6H_5F)_2][CHB_{11}Cl_{11}]$, **1**, were obtained in an attempt to synthesize $[Cl_2Ga][CHB_{11}Cl_{11}]$ according to eq 1.

$$GaCl_3 + [Et_3Si][CHB_{11}Cl_{11}] \rightarrow [Cl_2Ga][CHB_{11}Cl_{11}] + Et_3SiCl \qquad (1)$$

The crystal structure (Figure 1) showed some residual electron density close to the gallium center in the approximate region where hydride substituents would be expected. However, the failure to detect a gallium hydride signal in the ^1H NMR spectrum or an absorption around 2000 cm^{-1} (ν_{Ga-H}) in the IR spectrum,[19] followed by the detection of a signal in the ^{71}Ga NMR spectrum at −703 ppm, which is in the typical region for gallium(I) compounds,[2] convinced us that we had indeed isolated a gallium(I) species. As this finding was supported by preliminary DFT calculations, which indicated that the

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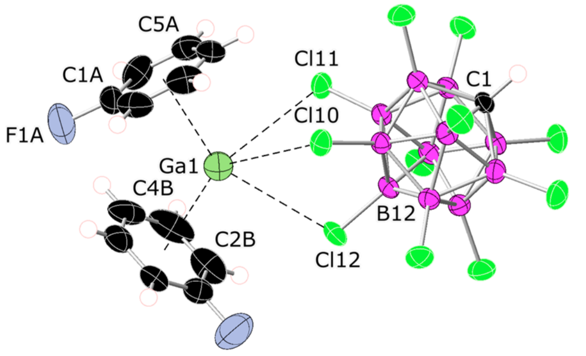


Figure 1. Structure of **1** (50% ellipsoids). Selected distances (Å) and angles (deg): Ga(1)···centroid = 2.721(2), 2.948(1); Ga(1)···Cl(10) = 3.400(2); Ga(1)···Cl(11) = 3.397(2); Ga(1)···Cl(12) = 3.353(3), and centroid−Ga(1)−centroid = 119.8°.

gallium(I) cation $[Ga(C_6H_5F)_2]^+$ was more stable than the gallium(III) cation $[H_2Ga(C_6H_5F)_2]^+$, an optimization of the synthetic procedure was developed, as well as an extension to additional species with the weakly coordinating anions (WCAs) $[B(C_6F_5)_4]^-$ and $[NTf_2]^-$.

Hydrosilanes have long been known to convert chlorogallanes into hydrogallanes at or below room temperature, as according to eq 2.[20]

$$GaCl_3 + Me_3SiH \rightarrow 1/2(HGaCl_2)_2 + Me_3SiCl \qquad (2)$$

It is likely that residual Et_3SiH from the synthesis of the silylium ion reagent $[Et_3Si][CHB_{11}Cl_{11}]$ caused the formation of an intermediate $[H_2Ga]^+$ ion, which then eliminated H_2 to afford compound **1**. In order to test this hypothesis, the reaction was performed as above (see eq 1) followed by the addition of excess Et_3SiH, which gave the target compound in 48% yield in the form of colorless crystals. A variation of this procedure, the addition of the silylium salt to in-situ generated $(H_2GaCl)_2$[19] in the presence of excess Et_3SiH, avoids the presence of an intermediate and likely highly reactive $[Cl_2Ga][CHB_{11}Cl_{11}]$, leading to an overall cleaner product in 42% yield. It is not clear at this point if the silylium ion abstracts a chloride or hydride ion from $(H_2GaCl)_2$ (Scheme 1). In the latter case, the excess Et_3SiH would convert the intermediate $[HGaCl]^+$ into $[H_2Ga]^+$, which then undergoes reductive elimination to form the arene-coordinated Ga(I) cation **1**.

For comparison, we have also obtained $[Ga(C_6H_5Br)][CHB_{11}Cl_{11}]$, **2**, by the Slattery−Krossing method[2] (eq 3) in analogy to the synthesis of the indium compound $[In(C_6H_5Br)_{1.5}][CHB_{11}Cl_{11}]$.[21]

$$Ga + Ag[CHB_{11}Cl_{11}] \xrightarrow[-Ag]{\Delta, C_6H_5Br} \underset{\mathbf{2}}{[Ga(C_6H_5Br)][CHB_{11}Cl_{11}]} \qquad (3)$$

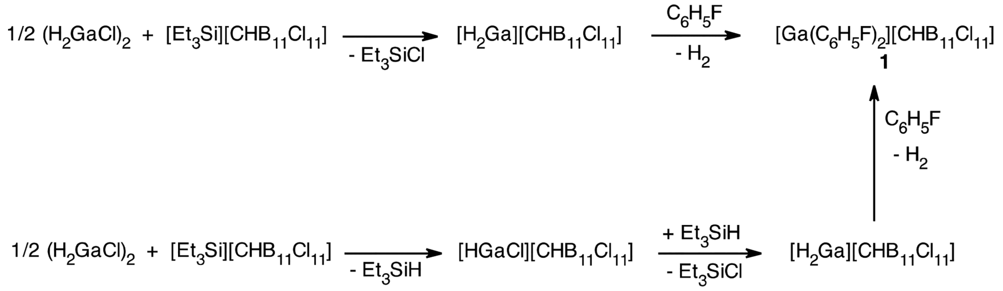
Given the relative ease with which compound **1** can be prepared through the reductive elimination route, we were interested if this method could be extended to more readily available counterions such as $[B(C_6F_5)_4]^-$ and $[N(SO_2CF_3)_2]^-$. For both anions, suitable precursors such as $[Ph_3C][B(C_6F_5)_4]$ and $HN(SO_2CF_3)_2$ are commercially available. The Slattery−Krossing method may not be ideal to use with $Ag[B(C_6F_5)_4]$ due to the latter's thermal lability[22] and its multistep synthesis.[23] On the other hand, the sensitivity of the $[B(C_6F_5)_4]^-$ anion toward strong Lewis acids could have been detrimental in the presence of the Lewis acid $[H_2Ga]^+$. Fortunately, our new method, the addition of $[Ph_3C][B(C_6F_5)_4]$ to freshly prepared $(H_2GaCl)_2$ in the presence of excess Et_3SiH (eq 4), afforded the target compound, $[Ga(Ph_3CH)][B(C_6F_5)_4]$, **3**, after crystallization, albeit in low yields (19%).

$$1/2(H_2GaCl)_2 + [Ph_3C][B(C_6F_5)_4] \xrightarrow[-Et_3SiCl]{+Et_3SiH} \underset{\mathbf{3}}{[Ga(Ph_3CH)][B(C_6F_5)_4]} + H_2 \qquad (4)$$

The mother liquor contained numerous compounds derived from the decomposition of the $[B(C_6F_5)_4]^-$ anion as shown by ^{19}F NMR spectroscopy (see Figure S15). As the silylium salt $[Et_3Si][B(C_6F_5)_4]$ was not isolated in this synthesis, the triphenylmethane side product was found to be coordinated to the gallium(I) cation due to its higher basicity compared to fluorobenzene.

Several attempts were made to prepare $[Ga(arene)_n][N(SO_2CF_3)_2]$, and the best procedure appears to be a two-step approach (eqs 5 and 6). First, the reaction of $(H_2GaCl)_2$ with $HN(SO_2CF_3)_2$ in hexanes in the presence of excess Et_3SiH resulted in the formation of a colorless, hexane insoluble solid, which is tentatively identified as $H_2GaN(SO_2CF_3)_2$, **4**, based on NMR and IR data. The ^1H NMR spectrum shows a strong broad signal at 4.68 ppm and the IR spectrum a peak at 2080 cm^{-1}, both indicative of the Ga−H unit. For example, the compound $H_2Ga(C_6H_4\text{-}2\text{-}CH_2NMe_2)$, which also features a bidentate monoanionic substituent, displays the Ga−H ^1H NMR signal at 5.59 ppm and the Ga−H stretch at 1856 cm^{-1}.[24] The significantly higher frequency of the Ga−H stretch for **4** may be explained by the higher positive charge on the gallium center, and this finding is also supported by DFT calculations (see below and in the Supporting Information). The corresponding data for $(H_2GaCl)_2$ are 5.46 ppm and 2021 cm^{-1}.[19] Solutions of compound **4** in C_6D_6 slowly eliminate H_2

Scheme 1. Possible Pathways for the Formation of 1



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at room temperature, and after several hours the ^{71}Ga NMR spectrum shows a weak peak at −645 ppm ($w_{1/2}$ = 1100 Hz), indicating the presence of Ga(I) in an asymmetric environment. A microcrystalline solid of a compound tentatively identified as $GaN(SO_2CF_3)_2$, **5**, was obtained after leaving a hexane/C_6D_6 solution of **4** standing at room temperature for 4 weeks. This reaction can be accelerated by heating at 60−90 °C, but it is accompanied by the formation of a fine gray precipitate and an eventual weakening of the Ga(I) ^{71}Ga NMR signal, likely due to decomposition of **5**.

$$1/2(\mathrm{H_2GaCl})_2 \xrightarrow[-\mathrm{H_2}/-\mathrm{Et_3SiCl}]{+\mathrm{Et_3SiH}/+\mathrm{HN(SO_2CF_3)_2}} \underset{\mathbf{4}}{\mathrm{H_2Ga[N(SO_2CF_3)_2]}} \quad (5)$$

$$\underset{\mathbf{4}}{\mathrm{H_2Ga[N(SO_2CF_3)_2]}} \xrightarrow[-\mathrm{H_2}]{\Delta} \underset{\mathbf{5}}{\mathrm{Ga[N(SO_2CF_3)_2]}} \quad (6)$$

Interestingly, the putative intermediates $[H_2Ga(arene)_n]$-[WCA] spontaneously decompose to the gallium(I) compounds **1** and **3** for $[WCA]^-$ = $[CHB_{11}Cl_{11}]^-$ and $[B(C_6F_5)_4]^-$; whereas, the more basic triflimide counterion stabilizes the gallium(III) hydride **4**, and conversion to the gallium(I) species **5** requires energy. This is also supported by DFT calculations (vide infra).

The structures of **1** (Figure 1) and **3** (Figure 2) were determined by single crystal X-ray diffraction and show that the gallium(I) centers are coordinated by two arenes in a slightly distorted η^6 fashion and have also moderate (**1**, Ga···Cl = 3.353−3.400 Å) and weak (**3**, Ga···F = 3.123 Å) contacts to the counterion. This bent sandwich geometry is typical for many gallium(I) arene complexes,[13,25] including the long-known compounds $[Ga(benzene)_2][GaCl_4]$[26] and $[Ga(C_6H_3Me_3)_2][GaCl_4]$,[27] as well as the more recently reported $[Ga(C_6H_5F)_2][Al\{OC(CF_3)_3\}_4]$[2,3] and $[Ga(C_6H_3Me_3)_2][Al\{OC(CF_3)_3\}_4]$.[3] The gallium environment in compound **3** is similar to that in $[Ga(C_6H_5F)_2][Al\{OC(CF_3)_3\}_4]$,[2,3] whereas the Ga···C and Ga···Cl distances in compound **1** are closer to those of the classic $[Ga(benzene)_2][GaCl_4]$[26] (Table S3), reflecting the higher basicity of the carborate anion.[28] Closer Ga···X contacts lead to longer Ga···C distances and narrower centroid−Ga−centroid angles. On the other hand, compound **1** is rather robust, whereas compound **3** can experience anion decomposition under harsh conditions (vide infra); $[Ga(benzene)_2][GaCl_4]$ is known to suffer from various decomposition modes dependent on conditions.[13] In compound **3**, each gallium center is coordinated to phenyl groups from two different triphenylmethane molecules, leading to a coordination polymer (Figure S47) similar to the silver compound $[Ag(Ph_3CH)][MeCB_{11}F_{11}]$.[29] In addition, there are two additional phenyl groups in contact with the gallium center in an η^2 fashion with rather long average distances of 3.461 and 4.128 Å, resulting in an overall bowl-shaped environment for the gallium center (Figure S48).

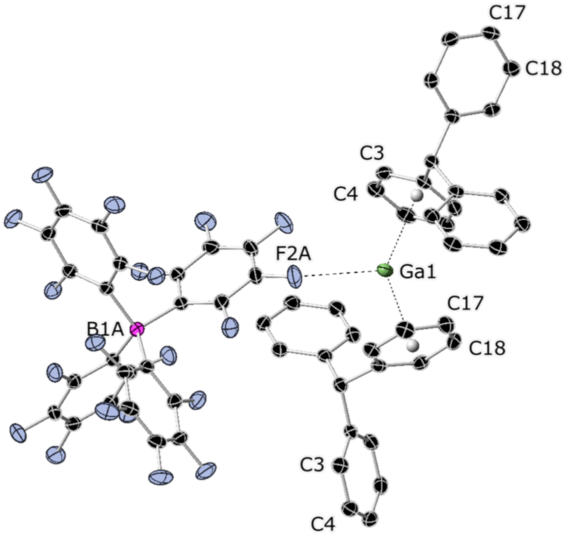

Figure 2. Structure of **3** (50% ellipsoids). H-atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ga(1)···centroid = 2.601(2), 2.675(2); Ga(1)···F(2A) = 3.123(2); and centroid−Ga(1)−centroid = 140.7°.

Compounds **1**−**3** are readily soluble in moderately polar aromatic solvents such as fluoro- and bromobenzene. As long as the coordination environment of gallium is symmetrical, ^{71}Ga NMR spectroscopy is an excellent analytical tool with a rather high sensitivity; solutions of **1**−**3** with concentrations of ca. 10−20 mM give rise to strong signals in the Ga(I) region[2,25] of −650 to −750 ppm and peak widths of 150−300 Hz.

A preliminary computational investigation of the stabilities of the cations $[Ga(arene)_2]^+$ (arene = C_6H_6, C_6H_5F) and *syn* and *anti* $GaN(SO_2CF_3)_2$, **5**, was conducted with respect to the precursors $[H_2Ga(arene)_2]^+$ and *syn* and *anti* $H_2GaN(SO_2CF_3)_2$, **4**, using density functional theory calculations. No interactions with the anion were assumed for the cation calculations, and the choice of the arene-coordinated precursors is based on the existence of an arene-coordinated cation in $[(2,6\text{-}Mes_2C_6H_3O)_2Al]^+$[30] and the fact that the former represent a minimum on the potential energy surface. For the identification of the structural minima, geometry optimizations were performed using the B97-D3(BJ) exchange−correlation functional[31,32] and the def2-SV(P) basis set,[33] starting from random initial orientations of the fragments. The energetic results have been further refined using single-point calculations on the optimized structures using the ωB97M-V[34] and the MN15 functionals[35] with the def2-TZVP basis set.[33] The energetic results show that $[Ga(C_6H_6)_2]^+$ and $[Ga(C_6H_5F)_2]^+$ are more stable than the corresponding gallium(III) hydride cations by 11.4 and 10.6 kcal/mol, respectively (see Table S4). The results also reflect the experimentally observed higher stability of the gallium(III) triflimide **4** over the gallium(I) species **5** by 9.4 kcal/mol. Furthermore, the calculated data for the $[Ga(C_6H_5F)_2]^+$ cation agree very well with the XRD data for **1** (see Table S3), and the calculated harmonic frequency for the IR active asymmetric Ga−H stretch (2092 cm^{-1}) for the *syn* isomer of **4** is close to the observed one (2080 cm^{-1}).

An exploratory reactivity study focused on the activity of compounds **1** or **2** and **3** as catalysts for the polymerization of 2,4,4-trimethyl-1-pentene and the hydrosilylation of benzophenone, 1-hexene and CO_2. The Krossing group has shown that $[Ga(arene)_2][Al\{OC(CF_3)_3\}_4]$ compounds are active catalysts for the polymerization of isobutene to highly reactive polyisobutylene.[3,4] For operational simplicity the olefin 2,4,4-trimethyl-1-pentene (bp = 101 °C) was chosen here as an alternative to isobutene (bp = −7 °C), although it is known to resist polymerization.[36] Both compounds **1** and **3** readily catalyzed an exothermic reaction that led to a mixture of dimers, trimers, and tetramers still possessing a double bond (see Figures S21−S26). Furthermore, a strong Ga(I) signal is detected in the ^{71}Ga NMR spectra after three cycles, indicating the robustness of the system. Benzophenone is rapidly (30 min for **3**) reduced to diphenylmethane using Et_3SiH and a catalyst loading of 1%, and the intermediate $Ph_2C(H)OSiEt_3$ is not detected even in a 1:1 Ph_2CO:Et_3SiH reaction. As before, a Ga(I) signal is detected in the ^{71}Ga NMR spectra of the reaction mixtures after two cycles. Interestingly, compound **3** appears to be the more active catalyst, possibly a result of the lower basicity of the $[B(C_6F_5)_4]^-$ anion and its higher solubility in the C_6D_6/C_6D_5Br solvent mixture employed. The hydrosilylation of 1-hexene with Et_3SiH and 1% catalyst loading leads to the anti-Markovnikov product; however, several hours of heating at 70−90 °C is required. Despite the high activity in the benzophenone reduction, no CO_2 reduction was observed even after 27 h at 80−82 °C. Instead, a partial scrambling of the Et-Si substituents was observed to afford Et_4Si and Et_2SiH_2, and the $[B(C_6F_5)_4]^-$ anion in compound **3** was partially decomposed during the reaction.

■ CONCLUSION

In conclusion, cationic gallium(III) hydrides $[H_2Ga]^+$ are unstable with respect to arene-coordinated gallium(I) cations $[Ga(arene)_n]^+$, and this reaction can serve as a convenient entry into Ga(I) chemistry. Based on experimental and computational results, the presence of a weakly coordinating counterion such as $[CHB_{11}Cl_{11}]^-$ or $[B(C_6F_5)_4]^-$ results in an exothermic reaction, whereas more basic counterions such as $[N(SO_2CF_3)_2]^-$ or even Cl^- require energy for the Ga(III) to Ga(I) conversion. Furthermore, compounds **1** and **3** were active catalysts for the oligomerization of 2,4,4-trimethyl-1-pentene and the hydrosilylation of benzophenone.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b02136.

> Experimental section; NMR, IR, and mass spectra of compounds **1**−**5**; reaction mixtures and products; and X-ray data and computational details (PDF)

Accession Codes

CCDC 1941357−1941358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rwehmsch@fit.edu.

ORCID

Rudolf J. Wehmschulte: 0000-0003-0719-0620

Notes

The authors declare no competing financial interest.

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