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Hydrides Hot Paper

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A Brønsted Acidic Gallium Hydride: Facile Interconversion of NNNN-Macrocycle Supported $[Ga^I]^+$ and $[Ga^{III}H]^2+$

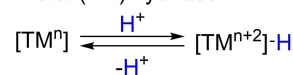
Louis J. Morris, Priyabrata Ghana, Thayalan Rajeshkumar, Ambre Carpentier, Laurent Maron,* and Jun Okuda*

Abstract: Protonolysis of $[Cp^*M]$ ($M = Ga, In, Tl$) with $[(Me_4TACD)H][BAR_4^{Me}]$ ($Me_4TACD = N, N', N'', N'''$ -tetramethyl-1,4,7,10-tetraazacyclododecane; $[BAR_4^{Me}]^- = [B\{C_6H_3-3,5-(CH_3)_2\}_4]^-$) provided monovalent salts $[(Me_4TACD)M][BAR_4^{Me}]$, whereas $[Cp^*Al]_4$ yielded trivalent $[(Me_4TACD)AlH][BAR_4^{Me}]_2$. Protonation of $[(Me_4TACD)Ga][BAR_4^{Me}]$ with $[Et_3NH][BAR_4^{Me}]$ gave an unusually acidic ($pK_a(CH_3CN) = 24.5$) gallium(III) hydride dication $[(Me_4TACD)GaH][BAR_4^{Me}]_2$. Deprotonation with IMe_4 (1,3,4,5-tetramethyl-imidazol-ylidene) returned $[(Me_4TACD)Ga][BAR_4^{Me}]$. These reversible processes occur with formal two-electron oxidation and reduction of gallium. DFT calculations suggest that gallium(I) protonation is facilitated by strong coordination of the tetradentate ligand, which raises the HOMO energy. High nuclear charge of $[(Me_4TACD)GaH]^2+$ facilitates hydride-to-metal charge transfer during deprotonation. Attempts to prepare a gallium(III) dihydride cation resulted in spontaneous dehydrogenation to $[(Me_4TACD)Ga]^+$.

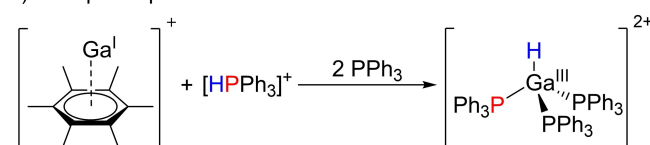
Introduction

The first well-defined transition metal (TM) hydride complex $[H_2Fe(CO)_4]$ was synthesized by Hieber and Leutert over 90 years ago, by protonation of $[Fe(CO)_4]^{2-}$ with formal two-electron oxidation of the metal center per proton.^[1] Late transition metal hydrides containing electron-withdrawing ligands display Brønsted acidity, such that deprotonation results in formal two-electron reduction of the metal center (Scheme 1a).^[2] Pertinent to this, the acid-base chemistry of TM-hydrides has been studied in some detail,

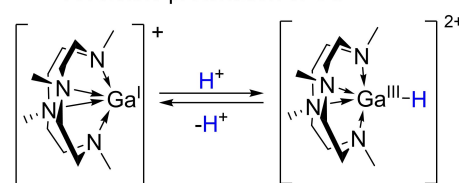
a) Acidic transition metal (TM) hydrides



b) Phosphine-promoted oxidative addition at Ga^+



c) This work: reversible protonation of Ga^+



Scheme 1. a) Brønsted acid–base chemistry at transition metals.^[2,3]

b) Oxidative addition (protonation) of a phosphonium salt at a gallium(I) cation reported by Krossing et al.^[12] c) Brønsted acid–base chemistry at gallium reported herein.

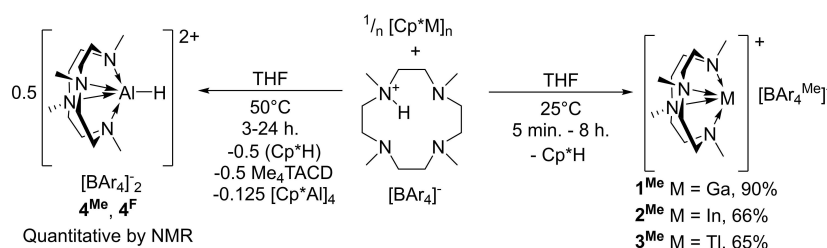
and acidity quantified using the pK_a scale in aprotic solvents.^[3] Brønsted acidity is closely related to electro-negativity, the extent of M–H bond polarization and covalency, and thermodynamic stability of the low-valent conjugate base. Among the most commonly employed sources of nucleophilic hydride are those of the lighter Group 13 elements.^[4] They do not react as Brønsted acids on account of a polarized bond $M^{\delta+}-H^{\delta-}$ and low thermodynamic stability of the corresponding boryl, alumanyl, or gallyl conjugate base. Reactions with bases tend to result in ate-complexes.^[5]

The ability for the main group elements to display “transition metal like” behavior has attracted considerable attention in recent years, as part of a wider effort to become less dependent upon scarce and expensive precious metal catalysts.^[6] Although significant progress has been made regarding oxidative addition of a plethora of σ -bonds,^[7] incorporation of such reactivity into two-electron redox catalytic cycles remains a significant challenge.^[7,8] Gallium occupies a special position in the Group 13 series. It has the highest Pauling electronegativity ($\chi = 1.81$) of the Group 13 metals^[9] and the poorly shielding qualities of the filled 3d subshell results in the “Scandide Contraction”, which leads to a comparable ionic radius to that of aluminium.^[5a,10]

[*] Dr. L. J. Morris, Dr. P. Ghana, Prof. Dr. J. Okuda
 Institute for Inorganic Chemistry
 RWTH Aachen University
 52062 Aachen (Germany)
 E-mail: jun.okuda@ac.rwth-aachen.de

Dr. T. Rajeshkumar, A. Carpentier, Prof. Dr. L. Maron
 CNRS, INSA, UPS, UMR 5215, LPCNO
 Université de Toulouse
 135 Avenue de Rangueil, 31077 Toulouse (France)
 E-mail: laurent.maron@irsamc.ups-tlse.fr

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Scheme 2. Reaction between $[\text{Cp}^*\text{M}]$ and $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4]$. $\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$; $\text{Ar} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$ (**4^F**), $3,5\text{-(CH}_3)_2\text{-C}_6\text{H}_3$ (**1-4^{Me}**). Yields refer to isolated crystalline product.

Importantly, this effect also lowers the energy of the $4s$ orbital and thus renders the $+1$ oxidation state relatively thermodynamically accessible, compared to aluminium. The HOMO energy can be further decreased by installing cationic charge, such that gallium(I) cations tend to behave as soft Lewis acids and only display weakly basic behavior in the presence of neutral σ -donor ligands.^[11] Consequently, an appropriate ligand may bring the $+1$ and $+3$ oxidation states close enough in energy to allow two-electron redox cycling.

Very recently, Krossing et al. demonstrated that $\text{Ga}[\text{Al}(\text{OR}^{\text{F}})_4]$ ($\text{OR}^{\text{F}} = \text{OC}(\text{CF}_3)_3$) can be activated by the coordination of phosphine ligands, thus raising the HOMO sufficiently to allow protonation by $[\text{HPPH}_3]^+$ through formal oxidative addition of a P-H bond (Scheme 1b).^[12] The resulting dicationic gallium(III) hydride $[\text{HGa}(\text{PPh}_3)_3][\text{Al}(\text{OR}^{\text{F}})_4]_2$ was the first of its kind, although the nature and reactivity of the hydride were not discussed in detail. We recently showed that oxidative addition and reductive elimination of the $[\text{AlH}_2]^+$ fragment to a neutral gallium(I) complex was finely balanced, such that σ -donor strength of the supporting ligands and solvent could steer the heterobimetallic system towards a formally $\text{Ga}^{\text{II}}\text{-Al}^{\text{II}}$ dimer, or discrete Ga^{I} and Al^{III} monomers.^[13] By analogy to transition metal hydrides, we wished to explore the viability of redox cycling in mononuclear Group 13 hydrides by protonation/deprotonation reactions at a cationic metal center (Scheme 1c). The versatile macrocyclic ligand Me_4TACD (N,N',N'',N''' -tetramethyl-1,4,7,10-tetraazacyclododecane) was chosen as a platform to systematically probe the acid-base chemistry of the Group 13 series from aluminum to thallium. In this contribution, we report the reversible protonation of the $[(\text{Me}_4\text{TACD})\text{Ga}]^+$ cation and experimentally and computationally compare it to homologous aluminium, indium, and thallium-based systems.

Results and Discussion

Previously, the groups of Cowley and Fischer prepared inverse sandwich cations $[\text{M}_2\text{Cp}^*]^+$ via protonolysis of $[\text{Cp}^*\text{M}]$ ($\text{M} = \text{Ga}, \text{In}$; $\text{Cp}^* = \text{C}_5\text{Me}_5^-$) with 0.5 equiv. of $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}_4^{\text{F}}]$ ($\text{BAR}_4^{\text{F}} = [\text{B}(\text{3,5-(CF}_3)_2\text{-C}_6\text{H}_3)_4]^-$) or $[(\text{toluene})\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, respectively.^[14] Similarly, $\text{In}[\text{O}_3\text{SCF}_3]$ can be prepared by protonolysis of $[\text{Cp}^*\text{In}]$ with triflic acid.^[15] Inspired by this work, we reacted $[\text{Cp}^*\text{M}]$

($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) with an equimolar quantity of $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4^{\text{Me}}]$ ($\text{BAR}_4^{\text{Me}} = [\text{B}(\text{3,5-(CH}_3)_2\text{-C}_6\text{H}_3)_4]^-$) in THF. The respective monovalent cation borate $[(\text{Me}_4\text{TACD})\text{M}][\text{BAR}_4^{\text{Me}}]$ (**1^{Me}**-**3^{Me}**) crystallized directly from the reaction mixture over the course of a few hours with elimination of Cp^*H (Scheme 2). Their molecular structure was confirmed by X-ray diffraction analysis as the anticipated charge separated ion pairs.

Compounds **1^{Me}** and **3^{Me}** crystallize in the chiral orthorhombic space group $Pna2_1$, with one ion pair in the asymmetric unit, whilst **2^{Me}** was solved in the monoclinic space group Pn , with two crystallographically independent anions and cations in the asymmetric unit. The crystal structure of the cationic part of **1^{Me}** is shown in Figure 1 (see Supporting Information for details and the crystal structures of **2^{Me}** and **3^{Me}**). In each case, the metal center is located at the apex of a square-based pyramid, projected above the N_4 -basal plane by a distance that increases with atomic number: 1.3007(15), 1.501(2)/1.521(2), 1.616(5) Å, **1-3^{Me}**, respectively. The value for the gallium cation is significantly smaller than that of the recently reported crown-ether complexes $[(12\text{-crown-4})\text{Ga}][\text{A}]$ ($\text{A} = [\text{GaCl}_4]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$; $d(\text{Ga-plane}) = 1.4375(7)$ Å, $1.4432(10)$ Å, respectively),^[16] suggesting stronger coordination of the Me_4TACD aza-crown. Consistent with lower charge-density, the Ga-plane distance and Ga-N bond lengths are significantly longer than those of the isoelectronic $[(\text{Me}_4\text{TACD})\text{Ge}]^{2+}$ cation reported by Reid and co-workers.^[17] The M-N bond lengths are consistent with previous examples of N-donor supported monovalent

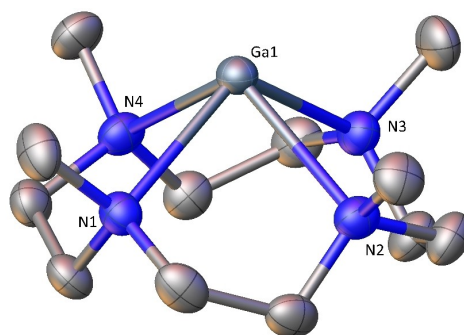


Figure 1. The cationic part of the crystal structure of compound **1^{Me}**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms are omitted for clarity.

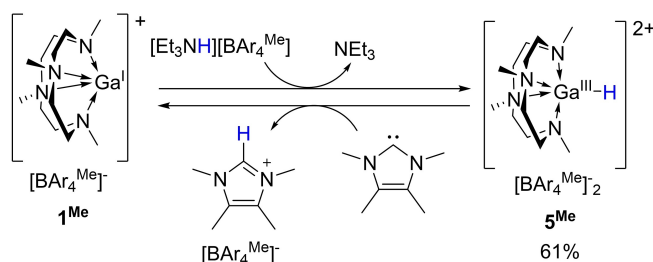
Group 13 cations^[18] and alternate in length, such that each cation contains two short and two long M–N bonds in a similar manner to the Ga–O bonds of [(12-crown-4)Ga][GaCl₄].^[16]

¹H NMR spectra of **1**^{Me}–**3**^{Me} in THF-*d*₈ showed multiplets associated with the AA'BB' spin system of the ligand ethylene bridges in the temperature range 283–333 K, indicating non-fluxional coordination to the metal center on the NMR timescale. Fine structure of the multiplet was only observed at room temperature for **1**^{Me}, with the heavier derivatives showing two broad and unresolved peaks. Similar size-effects were seen in the NMR spectra of the alkali metal silanide series [(Me₄TACD)M(SiPh₃)] (M=Li, Na, K, Rb, Cs).^[19] Further splitting of the CH₂ resonances into an ABMN spin system was observed at low temperatures as the dynamic ring-flipping motion becomes slow on the NMR timescale. The magnitude of splitting was more pronounced with increased ionic radius, although there was no correlation to the coalescence temperature. Temperature-dependent spin-spin coupling was observed between the ^{203/205}Tl nucleus (*S*=1/2) and the *N*-methyl ¹H (³*J*_{Tl-H}=9.0 Hz, 298 K) and ¹³C (²*J*_{Tl-C}=152.7 Hz, 298 K) nuclei in **3**^{Me}, whereas the analogous protons resonate as a singlet for the lighter metals. Strong temperature dependence of ^{205/203}Tl–X spin–spin coupling constants is well known,^[20] and room-temperature Tl–H coupling of a comparable magnitude has been previously observed in thallium-cryptate complexes.^[21] Compound **1**^{Me} was also characterized by ⁷¹Ga NMR spectroscopy, and whilst no resonance was detected in THF-*d*₈ solution, a very broad resonance ($\omega_{1/2}$ =3160 Hz) was detected at δ =–173 ppm in acetonitrile-*d*₃. This chemical shift is substantially downfield compared to “naked” Ga[Al(OR^F)₄] in fluorobenzene solution, (δ =–756 ppm).^[22] Coordination of weak σ - or π -donor ligands to Ga⁺ has been shown to result in downfield shifted signals, for example: δ =–520 ppm for Ga[Al(OR^F)₄] in toluene,^[22] δ =–448 ppm for Ga[Al(OR^F)₄] in THF,^[22] δ =–471 ppm for [(12-crown-4)Ga][GaCl₄] in toluene.^[16] The broader signal and further downfield chemical shift of **1**^{Me} may result from relatively strong Ga–Me₄TACD chelation by analogy to the similarly downfield resonance reported for [Ga(PPh₃)₃][Al(OR^F)₄] (δ =–144 ppm in *o*-F₂C₆H₄).^[22] The absence of metal-bound hydrides in **1**^{Me}–**3**^{Me} was confirmed by the 1:1 ligand/borate ratio in the ¹H NMR spectra and a lack of absorptions in the appropriate region of the solid-state IR spectra.

The analogous reaction of [Cp*Al]₄ with 4 equiv. of [(Me₄TACD)H][BAR₄^F] proceeded slowly in THF-*d*₈ at room temperature, but quantitative consumption of the proligand was observed after 3 h at 50 °C (Scheme 2). This was accompanied by elimination of half an equivalent each of Cp*H and uncomplexed Me₄TACD, with unreacted [Cp*Al]₄ clearly evident by analysis of the ¹H and ²⁷Al NMR spectra. The observed product ratios were rationalized by identification of the aluminium-containing product as the dicationic hydride [(Me₄TACD)AlH][BAR₄^F]₂ (**4**^F), by comparison to the separately synthesized complex (see below). Compound **4**^F displays a characteristic AA'BB' multiplet at δ =3.35 and 3.45 ppm and a ligand/borate ratio of 1:2. The hydride resonance was not detected by ¹H NMR spectro-

scopy, whilst the ²⁷Al NMR spectrum displayed a broad resonance at δ =107 ppm. When the reaction was repeated with 8 equiv. [(Me₄TACD)H][BAR₄^F], longer reaction times led to decomposition of the anion, but clean conversion to [(Me₄TACD)AlH][BAR₄^{Me}]₂ (**4**^{Me}) was achieved by using the non-fluorinated anion [BAR₄^{Me}][–] and was similarly identified by comparison of the in situ NMR spectrum to that of the separately synthesized complex (see below). These observations can be rationalized by considering the basicity of the putative [(Me₄TACD)Al]⁺ cation, which may be readily protonated by a second equivalent of [(Me₄TACD)H]⁺ to provide the observed dicationic aluminum hydride [(Me₄TACD)AlH]²⁺.

By analogy to the synthesis of high valence transition metal hydrides by protonation and the observed formation of **4** from [Cp*Al]₄, addition of a further equiv. of H⁺ to the heavier monovalent cations **1**^{Me}–**3**^{Me} could be envisaged to provide [M^{III}H]²⁺ dications with formal two-electron oxidation of the metal center. Dissolution of the gallium cation **1**^{Me} and [Et₃NH][BAR₄^{Me}] in THF-*d*₈ at room temperature provided selective conversion to a new species **5**^{Me}, within 5 min (Scheme 3). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated THF solution at room temperature and provided structural confirmation of **5**^{Me} as the dicationic gallium(III) hydride [(Me₄TACD)GaH][BAR₄^{Me}]₂ (Figure 2). By contrast, **3**^{Me} and **4**^{Me} were unreactive towards [Et₃NH][BAR₄^{Me}], and prolonged heating merely resulted in decomposition of the borate anion.



Scheme 3. Interconversion of **1**^{Me} and **5**^{Me}. Yield refers to isolated yield after crystallization. Reactions are quantitative as determined by in situ ¹H NMR spectroscopy.

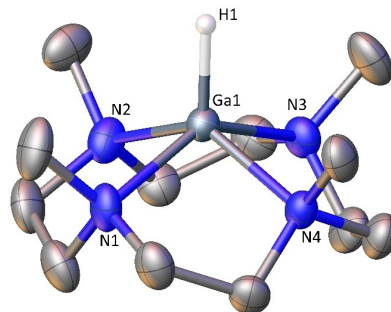


Figure 2. The dicationic part of the crystal structure of **5**^{Me}. Thermal ellipsoids are shown at the 50% level and hydrogen atoms are omitted except for the gallium-bound hydride.

Compound **5^{Me}** crystallizes in the monoclinic space group $P2_1/n$ with two anions, one dication, and 6 molecules of THF per asymmetric unit. The five-coordinate gallium center adopts a square-pyramidal geometry ($\tau_5=0.03$)^[23] with the nitrogen donors defining the basal plane and a terminal hydride occupying the apical coordination site (Figure 2). Two-electron oxidation of the gallium center results in contraction of the Ga–N bonds by approximately 0.33 Å, with the metal center located 0.755(1) Å above the basal plane defined by the four nitrogen atoms, compared to 1.3007(15) Å for **1^{Me}**. Consequently, the sum of N–Ga–N angles in **5^{Me}** is 330.48°, compared to 293.32° for **1^{Me}**. The hydride was located and freely refined, and the Ga–H bond length of 1.49(2) Å is the same, within experimental error, as that of [HGa(PPh₃)₃][Al(OR^F)₄]₂ (1.48(3) Å).^[12] The ¹H NMR spectrum in THF-*d*₈ is strongly reminiscent of the congeneric aluminum complex **4^{Me}**, with the ligand CH₂ protons represented by a relatively narrow unresolved multiplet at $\delta=2.37$ ppm, and the NCH₃ environment by a sharp singlet at $\delta=2.18$ ppm. The hydride ligand resonates as a broad signal at $\delta=4.35$ ppm, similar to previously reported cationic gallium hydrides,^[24] but significantly up-field of that reported for [HGa(PPh₃)₃][Al(OR^F)₄]₂ in 1,2-C₆H₄F₂ ($\delta=6.65$ ppm).^[12] In acetonitrile-*d*₃, the hydride resonance is not visible but fine structure of the AA'BB' CH₂ multiplets can be resolved, presumably resulting from a higher degree of charge separation in the ion pair. Regardless of solvent, the ⁷¹Ga NMR spectra were devoid of detectable resonances. The solid-state IR spectrum showed a band at $\nu=1982$ cm⁻¹, assigned to the Ga–H absorption.

As noted by Crossing et al., the σ -donating ligand is key to raising the energy of the gallium(I) *s*-orbital sufficiently to react with an electrophile.^[11] Computational interrogation of [(12-crown-4)Ga]⁺ suggested rather weak Ga–O bonds, and le Baines and co-workers to suggest the unsuitability of their cation for small-molecule activation.^[16] With this in mind, the solution-phase (THF) electronic structures of the cations **1⁺**–**3⁺** and dicationic hydrides **4²⁺** and **5²⁺** were computationally interrogated at the DFT (B3PW91) level. Optimized geometries were in good agreement to the crystallographically determined structures. The calculated Ga–H bond length of 1.558 Å for **5²⁺** was, however significantly longer than that found by X-ray diffraction. The HOMO of **1⁺**–**3⁺** consists of a metal-centered lone pair residing in a predominantly *s*-type molecular orbital, whilst the LUMO consists of a vacant *p*-orbital (Figure 3a, b). This situation is highly reminiscent to that of [(12-crown-4)Ga]⁺,^[16] whereas [(18-crown-6)Ga]⁺ complexes display almost non-directional lone-pairs which are only weakly influenced by additional axial ligands.^[25] In line with the higher reactivity of the gallium derivative towards protons, the HOMO of **2⁺** was found -3.1 kcal mol⁻¹ lower in energy relative to that of **1⁺**. As expected, the analogous molecular orbital of **3⁺** is significantly lower in energy, at -23.1 kcal mol⁻¹, due to the strong inert-pair effect. The Wiberg Bond Indices (WBI's) for the metal-nitrogen bonds are in line with their dative nature, and decrease with increasing atomic number from ca. 0.13 (**1⁺**) to 0.11 (**2⁺**) and 0.09 (**3⁺**), reflecting lower Lewis acidity of the softer, heavier cations. This is also consistent with a higher natural

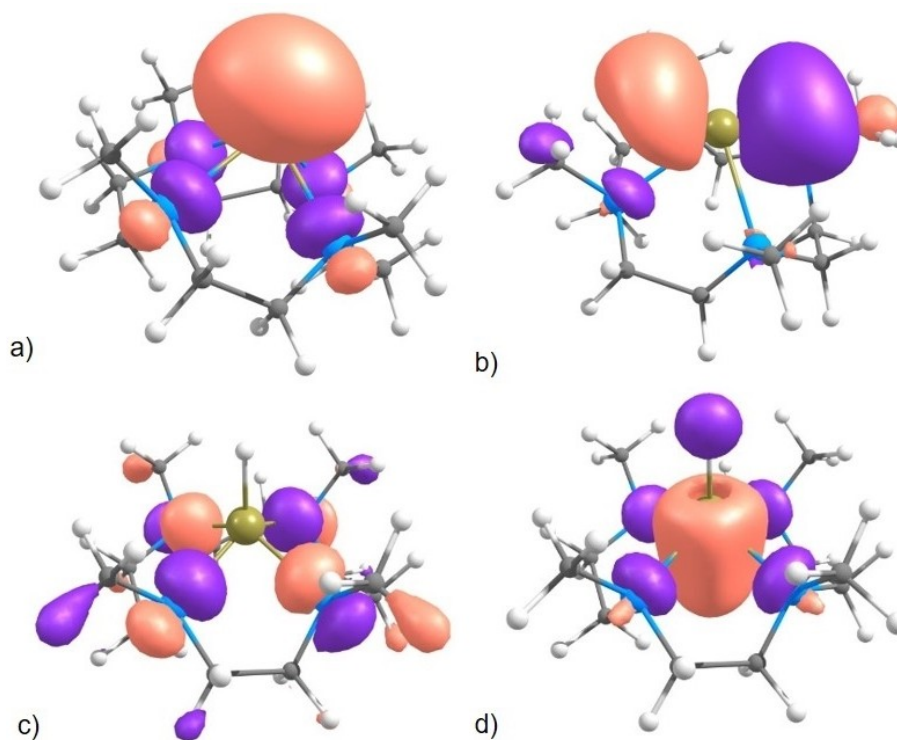


Figure 3. HOMO (a, c), and LUMO (b, d) molecular orbitals calculated for **1⁺** (a, b) and **5²⁺** (c, d).

charge on the heavier metal centers. NBO analysis of the dicationic hydrides 4^{2+} and 5^{2+} provided a similar picture in each case, with the metal hydride bonds strongly polarized towards H (73 %, 4^{2+} ; 72 %, 5^{2+}) and a WBI of around 0.77, consistent with a polar-covalent σ -bond. The HOMO of 5^{2+} was calculated to predominantly involve the filled nitrogen p -orbitals, whilst the LUMO can be described as the Ga–H σ^* antibonding orbital, which is expectedly polarized towards gallium (Figure 3c, d). Compared to 1^+ , the Ga–N WBI (ca. 0.23) and NPO charge of 1.64 at the metal center of 5^{2+} is in line with assignment of the +3-oxidation state. Formation of 5^{2+} by reaction of 1^+ and $[\text{Et}_3\text{NH}]^+$ was found to be endothermic by $3.3 \text{ kcal mol}^{-1}$, but inclusion of the $[\text{BAR}_4^{\text{Me}}]^-$ counterion results in a mildly exothermic calculated enthalpy $\Delta H_{\text{solv}} = -5.8 \text{ kcal mol}^{-1}$. The relatively accessible Ga–H σ^* and high nuclear charge of 5^{2+} prompted an investigation into the possible reactivity of the gallium hydride as a Brønsted acid.

To this end, the small N-heterocyclic carbene (NHC), IME_4 (1,3,4,5-tetramethyl-imidazol-ylidene) was added to a THF- d_8 solution of 5^{Me} . Analysis of the resulting colorless solution by ^1H NMR spectroscopy after 15 min at room temperature revealed quantitative reduction of the gallium(III) hydride to the gallium(I) cation 1^{Me} , with concomitant formation of the imidazolium borate salt $[\text{IME}_4\text{-H}][\text{BAR}_4^{\text{Me}}]$. The former was identified by X-ray diffraction of crystals obtained by slow evaporation of the reaction mixture, and also by the characteristic signals in ^1H NMR spectra of both the in-situ reaction mixture and isolated crystals. The IR spectrum of the isolated crystals was absent of the characteristic Ga–H absorption band. Formation of $[\text{IME}_4\text{-H}][\text{BAR}_4^{\text{Me}}]$ was confirmed by comparison of the in situ ^1H NMR spectrum to that of the separately synthesized compound, and displays a characteristic methine resonance at $\delta = 4.96 \text{ ppm}$. The aluminum hydride dication 4^{Me} appeared inert towards IME_4 and only traces of $[\text{IME}_4\text{-H}][\text{BAR}_4^{\text{Me}}]$ could be observed after heating at 40°C . Whilst hydrides of the late transition metals are well known to exhibit Brønsted acidity, polarization of the metal–hydride bond for more electro-positive metals means that this is an unusual reaction amongst the main group elements. Organotin(IV) hydrides

may be deprotonated by a strong base to form formally divalent stannanide anions.^[26] Furthermore, NHC-mediated reduction of heavier Group 14 and 15 dihydrides, dihalides, and hydridohalides is well established.^[27] We are, however, not aware of this method being applied to the Group 13 elements. Weaker bases were also explored: whilst amines such as NEt_3 , DABCO (1,4-diazabicyclo[2.2.2]octane), or pyrrolidine were unreactive, addition of a slight excess (1.3 equiv.) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to an acetonitrile- d_3 solution of 5^{Me} resulted in an equilibrium mixture of $\text{DBU}/[\text{DBU-H}]^+$ and $1^+ / 5^{2+}$. This provided the opportunity to estimate a pK_a value for the gallium hydride by comparison to the known value of $pK_a(\text{CH}_3\text{CN}) = 24.3$ for DBU.^[28] Dissolution of equimolar quantities of 1^{Me} and $[\text{DBU-H}][\text{BAR}_4^{\text{Me}}]$ in acetonitrile- d_3 similarly provided an equilibrium mixture of $\text{DBU}/[\text{DBU-H}]^+$ and $1^+ / 5^{2+}$, and the pK_a value of $1^+ / 5^{2+}$ was estimated as $pK_a(\text{CH}_3\text{CN}) = 24.5$ using NMR methods as described by Koppel and co-workers.^[29]

The reaction between 5^{2+} and IME_4 was investigated by computational methods at the DFT (B3PW91) level, using an SMD solvent model (THF). A reaction pathway was found, and proceeds via initial formation of a van der Waals encounter complex at $-2.1 \text{ kcal mol}^{-1}$, relative to the starting compounds (Figure 4). A transition state corresponding to direct attack of the NHC on the terminal gallium hydride was located at $+6.2 \text{ kcal mol}^{-1}$, and proceeds to the observed products 1^+ and $[\text{IME}_4\text{-H}]^+$ at $-28.1 \text{ kcal mol}^{-1}$. Whilst direct attack of the carbenic carbon on a hydride ligand of partial negative charge is counter-intuitive, further scrutiny of the transition state reveals an oblique approach of the NHC to the hydride, suggesting involvement of the NHC π -orbitals (Figure 4). The calculated Ga–H distance increases from 1.55 \AA in the van der Waals complex, to 1.75 \AA in the transition state consistent with weakening of the Ga–H bond, and transfer of proton to the carbenic carbon is also reflected by calculated Wiberg Bond Indices in the intermediate and transition state. Natural charges of the transition state reflect some charge transfer from the hydride (-0.23382) to gallium (1.42847), by comparison to the respective values in 5^{2+} (-0.38030 , 1.63796). It is notable

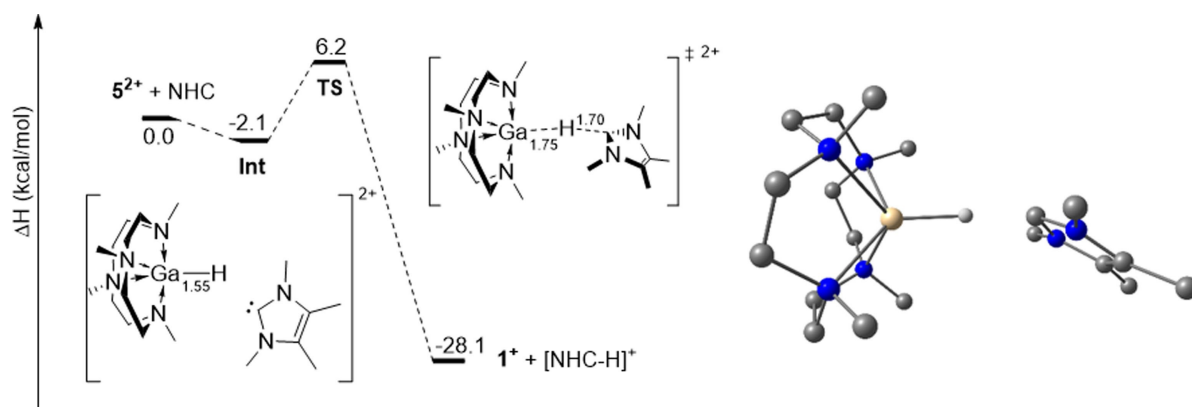


Figure 4. Calculated potential energy surface for the reaction between 5^{2+} and IME_4 with Ga–H and H–C bond lengths indicated (left); image of the transition state, showing the oblique approach of the NHC (right).

however, that the hydride retains a significant partial negative charge in the transition state.

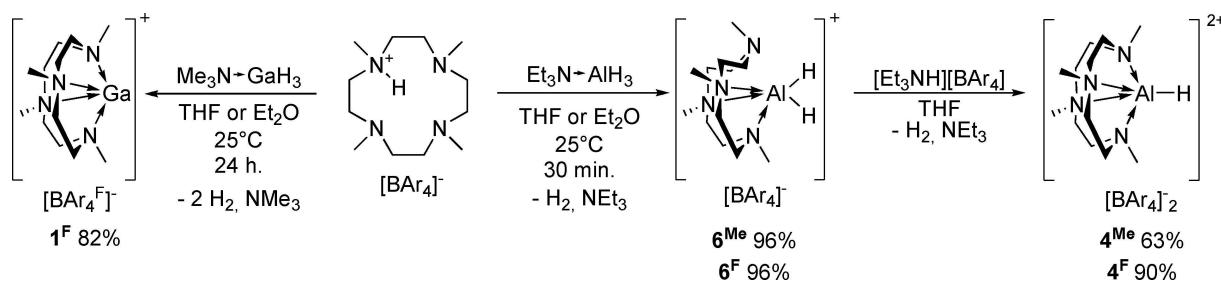
Having established the unusual behavior of the $[\text{Ga}^{\text{III}}\text{H}]^{2+}$ dication, we targeted the monocationic $[\text{Ga}^{\text{III}}\text{H}_2]^+$ species and its aluminum congener. Protonolysis of $\text{Et}_3\text{N}\cdot\text{AlH}_3$ with $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4]$ in THF or Et_2O smoothly yielded the monocationic aluminum(III) dihydrides $[(\text{Me}_4\text{TACD})\text{AlH}_2][\text{BAR}_4^{\text{Me}}]$ ($\mathbf{6}^{\text{Me}}$) and $[(\text{Me}_4\text{TACD})\text{AlH}_2][\text{BAR}_4^{\text{F}}]$ ($\mathbf{6}^{\text{F}}$) (Scheme 4). Compounds $\mathbf{6}^{\text{Me}}$ and $\mathbf{6}^{\text{F}}$ were characterized by single-crystal X-ray diffraction, NMR, IR spectroscopy, and elemental analysis, and display an unusual folded ligand conformation where one of the four methyl groups points towards the distal face of the cation (see Supporting Information, Figure S95). The corresponding Al1-N1 distance is elongated by as much as 37 pm relative to the other Al–N bonds, and a weaker bonding interaction was also suggested by DFT calculations (see Supporting Information for details). Although similar folded ligand conformations are common amongst the larger members of the aza-crown ligand family,^[30] examples of such folding with the 12-membered Me_4TACD ligand are limited to a minor component of $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-OCHO})_2]^{2+}$ in the solid state structure, which reverts to a symmetrical arrangement in solution.^[31] By contrast, compound $\mathbf{6}$ retains a folded conformation in THF- d_8 solution up to at least 70 °C, as shown by the complex array of CH_2 multiplets and three NCH_3 resonances (1:1:2 ratio) in the corresponding ^1H NMR spectra. The geometric constraints of the folded 12-membered macrocycle force the hydrides into a *cis*-arrangement. By contrast, the larger 14-membered macrocycle utilized in the closely related $[(\text{Me}_4\text{cyclam})\text{AlH}_2][\text{AlH}_4]$ ($\text{Me}_4\text{cyclam} = N,N',N'',N'''\text{-tetramethyl-1,5,8,12-tetraazacyclotetradecane}$) allows a relatively undistorted octahedral *trans*-dihydride geometry.^[32] Protonolysis of $\mathbf{6}^{\text{Me}}$ or $\mathbf{6}^{\text{F}}$ with the corresponding $[\text{Et}_3\text{NH}][\text{BAR}_4]$ salt eliminates NEt_3 and H_2 to cleanly provide the dicationic aluminum hydrides $\mathbf{4}^{\text{Me}}$ and $\mathbf{4}^{\text{F}}$, which were characterized by multinuclear NMR, IR spectroscopy, and elemental analysis.

The analogous reaction between $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4^{\text{F}}]$ and $\text{Me}_3\text{N}\cdot\text{GaH}_3$ in THF- d_8 also provided a single major Me_4TACD species of equimolar concentration to the borate anion after 24 h. at room temperature (Scheme 4). However, presence of a single N-methyl environment and AA'BB'-type multiplet centered at $\delta = 2.89, 2.72$ ppm in the ^1H NMR spectrum indicated a higher-symmetry ligand conformation.

Recrystallization from a saturated diethyl ether solution provided single crystals of the gallium(I) salt $[(\text{Me}_4\text{TACD})\text{Ga}][\text{BAR}_4^{\text{F}}]$ ($\mathbf{1}^{\text{F}}$), which was interpreted as the dehydrogenation product of the putative $[\text{GaH}_2]^+$ cation. Aside minor adjustments due to the different anion, the cationic part of the crystal structure of $\mathbf{1}^{\text{F}}$ is essentially identical to that of $\mathbf{1}^{\text{Me}}$. Compound $\mathbf{1}^{\text{F}}$ gives rise to a very broad resonance ($\omega_{1/2} = 5500$ Hz) centered at $\delta = -188$ ppm in the ^{71}Ga NMR spectrum in THF- d_8 . Wehmschulte and co-workers similarly described isolation of $\text{Ga}[\text{A}]$ salts (where $\text{A} = [\text{CHB}_{11}\text{Cl}_{11}]^-$ or $[\text{B}(\text{C}_6\text{F}_5)_4]^-$) by spontaneous dehydrogenation of transient $[\text{GaH}_2]^+$, generated by halide or hydride abstraction of a chlorogallane precursor.^[33] $[(\text{NHC})\text{GaH}_2]\text{I}$ salts were reported to decompose to intractable mixtures,^[24b] and partial dehydrogenation of gallium hydrides to isolable cluster-type species has also been documented.^[34] Aldridge and co-workers investigated the transition-metal mediated dehydrogenation of $[(\text{BDI})\text{GaH}_2]$ ($\text{BDI} = \text{HC}\{\text{C}(\text{CH}_3)\text{N}(2,6\text{-iPr-C}_6\text{H}_3)_2\}$) in quite some detail.^[35] Examples of clean dehydrogenation to a single well-defined product are, however, extremely rare and this reactivity highlights the fine balance between the mono- and trivalent oxidation states in cationic gallium chemistry.

Conclusion

In conclusion, we have explored the behavior of Group 13 cations throughout the aluminum to thallium series, supported by the macrocyclic Me_4TACD ligand. Monovalent cations of gallium ($\mathbf{1}^{\text{Me}}$), indium ($\mathbf{2}^{\text{Me}}$), and thallium ($\mathbf{3}^{\text{Me}}$) were readily prepared by protonolysis of corresponding pentamethylcyclopentadienyl derivatives with the cationic pro-ligand borate salt $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4^{\text{Me}}]$, whilst the analogous reaction of $[\text{Cp}^*\text{Al}]$ provided the dicationic aluminum(III) hydride $\mathbf{4}^{\text{Me}}$. Structural, spectroscopic, and computational analysis suggests relatively strong chelation of the monovalent cation, with somewhat weaker M–N bonds for the softer, heavier, and less Lewis acidic heavier derivatives. The relatively strong σ -donor properties of the polyamine ligand raise the energy of the gallium lone-pair sufficiently to allow protonation by the weak Brønsted acid $[\text{Et}_3\text{NH}][\text{BAR}_4^{\text{Me}}]$ with formal two-electron oxidation of the metal center, thus providing the dicationic gallium hydride $\mathbf{5}^{\text{Me}}$. Compound $\mathbf{5}^{\text{Me}}$ is unusually acidic, with an estimated



Scheme 4. Reaction of $[(\text{Me}_4\text{TACD})\text{H}][\text{BAR}_4]$ with $\text{Me}_3\text{N}\cdot\text{GaH}_3$ and $\text{Et}_3\text{N}\cdot\text{AlH}_3$ to form $\mathbf{1}^{\text{F}}$, $\mathbf{6}^{\text{F}}$ and $\mathbf{6}^{\text{Me}}$, and the protonolysis of $\mathbf{6}^{\text{F}}$ and $\mathbf{6}^{\text{Me}}$ to provide $\mathbf{4}^{\text{F}}$ and $\mathbf{4}^{\text{Me}}$.

pK_a of 24.5 in acetonitrile and as such, may be readily deprotonated by the strong neutral base IMe_4 with formal two-electron reduction of the metal center, to return $\mathbf{1}^{\text{Me}}$ and the corresponding imidazolium salt. Consistent with this, the putative gallium dihydride $[(\text{Me}_4\text{TACD})\text{GaH}_2][\text{BAr}_4^{\text{F}}]$ spontaneously eliminates H_2 to yield the gallium(I) salt $\mathbf{1}^{\text{F}}$, whereas the analogous aluminum dihydrides $\mathbf{6}^{\text{F}}$ and $\mathbf{6}^{\text{Me}}$ are stable with respect to dehydrogenation despite a rather strained ligand conformation. These results illustrate the potential for reversible redox cycling of the main group elements, where appropriate ligand choice and molecular charge can optimize the electronic structure. Given the rarity of main-group redox-cycling and the importance of proton-shuttling in organo- and bio-catalysis, we anticipate that these findings will stimulate further research into the development of main-group based redox catalysis.^[36,37]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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