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Novel Bi- and Trinuclear Gallium Halides and Hydrides with Acyclic and **Bicyclic Guanidinate Substituents: Synthesis and Reactivity**

Daniel Rudolf,^[a] Elisabeth Kaifer,^[a] and Hans-Jörg Himmel*^[a]

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We report on the synthesis and characterization of new molecular Ga halides and hydrides with acyclic guanidinate substituents with bicyclic guanidinate substituents. Acyclic guanidinates were found to adopt terminal bonding modes like in the dimeric Ga^{II} compound $[(iPr_2N)C(NiPr)_2GaI]_2$. In contrast, bicyclic guanidinates prefer bridging bonding modes. Hence, the reaction between Me₃N·GaH₃ and htbo (1,4,6-triazabicyclo[3.3.0]oct-4-ene) affords the binuclear Ga^{III} hydride $[H_2Ga(\mu-tbo)]_2$. This new hydride turned out to

Introduction

Guanidines and guanidinates are well established as versatile ligands or substituents in transition metal complexes as well as main-group and lanthanide element compounds.^[1–8] A recent highlight in the area of main-group element chemistry certainly represents the first synthesis of a stable dimeric Mg^I compound featuring sterically crowded guanidinate substituents and a direct Mg-Mg bond.^[9] Jones et al. also developed the synthesis and reactivity of monomeric aminidate and guanidinate Ga^I complexes which can be described as carbene analogues (see Scheme 1).^[10]



Scheme 1.

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Hydrides of the heavier group 13 elements were studied intensively in the past.^[11,12] They are not only of academic interest, but also applied for instance in CVD processes to form metal films or 13-15 materials such as GaN (cubic or hexagonal phases).^[11d,13] Our motivation to synthesize binuclear gallium hydrides by means of bridging guanidin-

[a] Anorganisch-Chemisches Institut,

Ruprecht-Karls-Universität Heidelberg,

Im Neuenheimer Feld 270, 69120 Heidelberg, Germany Fax: +49-6221-545707 E-mail: hans-jorg.himmel@aci.uni-heidelberg.de

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be unstable in solution at 25 °C, dihydrogen is slowly eliminated. In the solid state, however, the hydride is stable up to 80 °C. The thermodynamic properties of this and similar dehydrogenation reactions were studied my means of quantum chemical calculations. With $Ga_2H_5(\mu_3-O)(\mu-tbn)_2$ and $Ga_2H_5(\mu_3-O)(\mu-hpp)_{21}$ two new hydrides were synthesized which can be regarded as the first hydrolysis intermediates of binuclear Ga hydrides with bridging guanidinate substituents.

ate ligands initially arises from the results of matrix isolation experiments. These experiments showed that H_2 addition to the matrix-stabilized dimer Ga₂, leading (in a mildly exothermic reaction) to the D_{2h} -symmetric, binuclear Ga^I hydride Ga(μ -H)₂Ga, is associated with an only small barrier of ca. 30-50 kJ mol^{-1.[14]} This is a rare example of an oxidative addition of H_2 to a molecular E-E bond (E = non-carbon main-group element) with low activation barrier. We also reported on quantum chemical calculations indicating that the oxidative addition reaction of H₂ to the Ge-Ge bond of the hypothetical hydride HGeGeH ($D_{\infty h}$ symmetric isomer) to give H_2GeGeH_2 (C_{2h} symmetry) is significantly exothermic at standard conditions (ΔH^0 = -235 kJ mol⁻¹, MP2 calculations).^[15] A few years later Power et al. showed that digermynes and distannynes stabilized with bulky aryl substituents indeed add H₂ already at room temp. and 1 bar.^[16] Our efforts in the following years concentrated on the synthesis of new binuclear group 13 element (E) hydrides, in which the two elements are confined together in a distance which allows E-E bonding interactions with the aid of bridging substituents (see Scheme 2). Bicyclic guanidinates were found to be ideally suited for this purpose. We first studied boron hydrides, which are less reactive than gallium hydrides due to the stronger B-H bonding, and started our investigations with the adduct hppH·BH₃ (hppH = 1,3,4,6,7,8-hexahydro-2*H*-



Scheme 2. H₂ elimination and addition reactions with binuclear group 13 element (E) compounds featuring bridging substituents.

View this journal online at wileyonlinelibrary.com pyrimido[1,2-*a*]pyrimidine, see Scheme 3).^[17] Dehydrogenation of this adduct can be achieved elegantly catalytically in the presence of [Rh] at 80 °C in toluene solutions.^[18]



Scheme 3. Lewis structures of the guanidines used in this work for the synthesis of new gallium compounds.

The product $[H_2B(\mu-hpp)]_2$ was fully characterized. Further dehydrogenation occurs at 110 °C and leads to the doubly base-stabilized diborane(4) species $[HB(\mu-hpp)]_2$ exhibiting a roof-type structure. We also synthesized the dication $[(HNMe_2)B(\mu-hpp)]_2^{2+}$ with a direct B–B bond.^[19,20] Protonation of $[HB(\mu-hpp)]_2$ was shown to give the monocation $[B_2H_3(\mu-hpp)_2]^+$.^[21] The research was extended to other bicyclic guanidines (see Scheme 3), namely the two molecules htbo (1,4,6-triazabicyclo[3.3.0]oct-4-ene) and htbn (1,5,7-triazabicyclo[4.3.0]non-6-ene).^[22] We are currently studying catalytic H₂ addition to the B–B bond of $[HB(\mu-guanidinate)]_2$ species to regain $[H_2B(\mu-guanidinate)]_2$, and also other oxidative addition reactions to the B–B bond.

In the case of gallium chemistry, the adduct hppH·GaH₃ cannot be isolated, because it already eliminates dihydrogen at low temperatures (-78 °C).^[23] The product, [H₂Ga(µhpp)]₂, **1**, turned out to be also an extremely temperaturesensitive compound, which is only stable at low temperatures (≤ 0 °C) and represents an oily liquid at 0 °C. We were able to crystallize and structurally characterize the more stable derivative $[HClGa(\mu-hpp)]_2$, which turned out to melt at 10 °C and to decompose at 22 °C. Its decomposition leads presumably to elimination of H₂ and formation of $[ClGa(\mu-hpp)]_2$. The dehydrogenation pathways for such guanidine gallanes were additionally analysed by quantum chemical calculations.^[24] We also extended our work to the gallane adduct of the acyclic guanidine (Me₂N)₂C=NH and analysed its decomposition reactions.^[25] The adduct $(Me_2N)_2C=N(H)\cdot GaH_3$ turned out to decompose at relatively low temperatures (330–350 K). One of the decomposition products was crystallized and shown to be the Ga₇ cluster HN{[HGaNMe][H₂GaNC(NMe₂)₂]}₃GaH with an unusual cage-type assembly.

Herein we now report on the synthesis of new molecular Ga compounds with bicyclic and acyclic guanidinate substituents. Possible routes to molecular, binuclear Ga^{II} compounds featuring bridging guanidinate substituents and a direct Ga–Ga bond involve dehydrogenation of binuclear Ga^{III} hydrides or start directly with subvalent Ga compounds. As mentioned above, bicyclic guanidinate ligands were shown previously by us to yield binuclear Ga^{III} hydrides amenable to dehydrogenation to give binuclear Ga^{II} compounds.^[23] In continuation of this work, Ga hydrides were reacted herein with bicyclic guanidine ligands. On the other hand, mononuclear compounds are generally the products of reactions between acyclic guanidinate ligands and Ga^{III} compounds.^[9,26,27] To introduce a Ga–Ga bond, we therefore started directly with subvalent Ga compounds (namely "GaI" solutions) in the case of acyclic guanidinates.

Results and Discussion

Reactions with Acyclic Guanidinates

For the synthesis of acyclic guanidinates we started with "GaI" solutions prepared as described in the literature from Ga metal and I_2 .^[28] The exact composition and degree of association of these solutions is still unclear. They can be regarded as sources of Ga^I and Ga^{II}, the latter being formed by partial disproportionation of Ga^I. The two acyclic guanidines (*i*Pr₂N)C(N*i*Pr)(NH*i*Pr) and (*i*Pr₂N)C(NCy)(NHCy), see Scheme 3, were deprotonated with *n*BuLi and generally used without analysis. One of these Li guanidinate salts, however, crystallized from the solution together with two equivalents of diethyl ether, namely [(*i* $Pr)_2NC(NCy)_{2}LiOEt_2]_2$.

The structure of this dimeric assembly is visualized in Figure 1 (a). Each Li⁺ is fourfold coordinated, establishing one short [Li1–N1 198.7(3) pm] and two longer [221.4(3) pm] bonds to the guanidinate N atoms, and in addition a bond to an ether molecule [with Li–O bond lengths of 196.1(3) pm]. The structure is thus similar to that of other known dimeric Li guanidinates shown in Scheme 4.^[29] Unfortunately we were not able to isolate a product of the reaction between [(*i*Pr)₂NC(NCy)₂LiOEt₂]₂ and the Ga species present in the "GaI" solution.

The only species that was isolated in the form of a small number of crystals from the reaction mixture turned out to be $(GaI_2)_2(\mu$ -O){CyN=C(NHCy)(N*i*Pr₂)}₂, being either a product of partial hydrolysis or of reaction involving traces of neutral guanidine and O₂ (which oxidizes the Ga^I). Figure 1 (b) displays its molecular structure. Hydrogen bonding between the guanidine N–H groups and the bridging O atoms leads to formation of two six-membered heterocycles sharing an O edge.

On the other hand, the reaction between the Ga species present in the "GaI" solution and the Li salt of the guanidinate $(iPr_2N)C(NiPr)_2$ resulted in formation of the new binuclear Ga^{II} compound $[(iPr_2N)C(NiPr)_2GaI]_2$, **2** (see Figure 2). The Ga–Ga bond in **2** measures 239.52(9) pm. It can be directly compared to the Ga–Ga bond lengths in the two binuclear Ga^{II} molecules {GaI(Fiso)}₂ and {GaI(Piso)}₂, with the amidinate substituents RC(NAr)₂ (Ar = 2,6 $iPr_2C_6H_3$ and R = H in the case of Fiso and R = *t*Bu in the case of Piso).^[27] For these two molecules longer distances of



Figure 1. a) Molecular structure of $[(iPr)_2NC(NCy)_2LiOEt_2]_2$. Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Li1–N1 198.7(3), Li1–N2 221.4(3), Li1'–N2 206.2(2), Li1–OI 196.1(3), N1–C13 132.23(16), N2–C13 134.59(17), N3–C13 143.86(16), N1–Li1–N2 65.40(8), N2–Li1–OI 122.07(12); b) Molecular structure of Ga₂I₄O{CyN=C(NHCy)(NiPr₂)}₂ isolated in small amount. Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Ga–I1 255.13(7), Ga–I2 256.97(8), Ga–N1 195.0(3), Ga–O 173.2(5), N1–C1 134.4(5), N2–C1 133.9(5), N3–C1 137.0(5), N2–CO 282.1(3), I1–Ga–I2 106.36(3), N1–Ga–O 108.70(10), N1–C1–N2 117.6(3).

243.04(10) and 245.21(15) pm, respectively, were measured. It was shown previously that the Ga–Ga single bond can adopt a large range of values. Examples include the two compounds Ga₂[CH(SiMe₃)₂]₄ with a Ga–Ga bond length of 254.1(1) pm,^[30] and Li₂[Ga₂Cl₆] with a Ga–Ga bond length of 238.7(5) pm.^[31] In the Ga₂ dimer, quantum chemical (MP2) calculations found a Ga–Ga distance of 263 pm in the ³ Π_u state,^[32] which was verified as the electronic ground state with the aid of matrix isolation spectroscopy.^[33,34]



Figure 2. Molecular structure of $[(iPr_2N)C(NiPr)_2GaI]_2$, **2**. Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Ga1...Ga1' 2.3952(9), Ga1-I1 2.5667(6), Ga1-N1 1.970(3), Ga1-N2 1.965(3), N1-C1 1.339(4), N2-C1 1.331(4), N3-C1 1.408(4), I1-Ga1-Ga1' 114.46(2), N1-Ga1-Ga1' 122.52(9), N2-Ga1-Ga1' 123.72(9), N1-Ga1-N2 67.41(12), N1-C1-N2 109.7(3).

Reactions with Bicyclic Guanidines

Next we discuss the reactions between $Me_3N\cdot GaH_3$ and the bicyclic guanidines hppH, htbn and htbo (see Scheme 3). We started from rigorously purified samples of $Me_3N\cdot GaH_3$ (by sublimation)^[35] to avoid the presence of halide traces in the reaction mixture. htbn and htbo were prepared according to the literature.^[36]

hppH

As already mentioned, we reported previously on the reaction between Me₃N·GaH₃ and hppH.^[23] The likely product, $[H_2Ga(\mu-hpp)]_2$ is an extremely unstable compound that is difficult to characterize. However, we were able to isolate a first and much more stable product of its hydrolysis. In these experiments water was deliberately added to the reaction mixture, the molar ratio Me₃N·GaH₃/H₂O being 3:1 (see Scheme 5). From the reaction mixture a small quantity of a new product was obtained in crystalline form, which can be identified as the trinuclear Ga hydride Ga₃H₅(μ_3 -O)(μ -hpp)₂ (3).

In contrast to 1, compound 3 is stable at room temp. Its molecular structure in the crystalline phase is illustrated in Figure 3. A central oxygen atom is connected by three Ga atoms arranged in the form of a triangle. The two hpp units are located near two different edges of the Ga_3 triangle,



Scheme 4. Some structurally characterized Li guanidinates.



Scheme 5. Comparison between the reactions of hppH and 1,8-bis(trimethylstannyl)naphthalene with Ga^{III} compounds in the absence and presence of H₂O. (i) Me₃N•GaH₃, Et₂O, -78° C; (ii) H₂O, Me₃N•GaH₃, Et₂O, r.t. (iii) GaCl₃, toluene, -25° C (21% yield); (iv) H₂O, GaCl₃, toluene, -25° C (16% yield).



Figure 3. a) Molecular structure of the new trinuclear Ga hydride 3. Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Ga1-N1 193.3(4), Ga1-N4 192.3(4), Ga1-O1 185.8(3), Ga2-N2 197.2(4), Ga2-O1 189.5(3), Ga3-N5 196.4(4), Ga3-O1 188.8(3), N1-C1 133.8(6), N2-C1 135.5(5), N4-C8 134.9(6), N5-C8 133.7(6), N1-Ga1-N4 107.28(15), O1-Ga1-N1 101.59(15), O1-Ga1-N4 108.64(15), O1-Ga2-N2 103.11(14), O1-Ga3-N5 102.66(15); b) Molecular structure of the new trinuclear Ga hydride 4. Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Ga1-N1 1.944(4), Ga1-N4 1.927(4), Ga1-O1 1.846(3), Ga2-N2 1.951(4), Ga2-O1 1.883(3), Ga3-N5 1.962(4), Ga3-O1 1.887(3), N1-C1 1.340(6), N2-C1 1.324(6), N4-C7 1.331(6), N5-C7 1.311(6), N1-Ga1-N4 107.29(16), O1-Ga1-N1 104.20(15), O1-Ga1-N4 103.97(14), O1-Ga2-N2 100.67(15), O1-Ga3-N5 102.39(15).

adopting as expected a bridging bonding mode. One of the gallium atoms, Ga1, is thus bonded to both hpp-units. The five hydrogen atoms are end-on bonded to the Ga atoms, resulting in one GaH and two GaH₂ units. Compound 3 can be regarded as product of the reaction between 1 and "H₂GaOH" under dihydrogen elimination. It was shown previously that macrocycles containing several Lewis acidic centers can be prepared by hydrolysis of molecular group 13 element compounds. The manifold examples include the reaction between GaCl₃ and 1,8-bis(trimethylstannyl)naphthalene, which gave a binuclear GaIII compound under exclusion of water, and a trigallacycle with a µ₃-bonded O atom in the center (see Scheme 5), upon addition of H₂O (the yield being, like in our reaction, quite low).^[37] Like the bis(trimethylstannyl)naphthalene ligand, the guanidinate hpp is capable of bridging two Ga atoms. In the field of hydride chemistry, Rettig, Storr and Trotter obtained a polycyclic Ga, O, N cage compound [(GaH)₆- $(GaH_2)_2(\mu_3-O)_2(\mu_3-NCH_2CH_2NMe_2)_4(\mu-NHCH_2CH_2 NMe_2$)₂ containing μ_3 -bonded oxygen atoms and six GaH and two GaH₂ units by reaction between N,N-dimethylethylenediamine, Me₂NCH₂CH₂NH₂ and trimethylamine gallane, Me₃N·GaH₃.^[38] However, this hydride turned out to be extremely air-sensitive so that the authors could only report on the X-ray diffraction results. No yield or other forms of characterization were given, a deficiency that this compound unfortunately shares with ours. However, we will see in the following that a similar compound can be obtained reproducibly in larger amounts in the case of the 5-6 bicyclic guanidine htbn.

htbn

Similar to the situation with http, the hydride $[H_2Ga(\mu-tbn)]_2$ formed as the product of the reaction between

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Me₃N·GaH₃ and htbn turned out to be extremely temperature-sensitive, so that we were not able to characterize this species. However, when Me₃N·GaH₃ was treated with htbn in the presence of deliberately added H₂O (stoichiometric ratio htbn: $H_2O = 2:1$), crystals of a new, more stable compound were obtained. Figure 4 (a) shows its IR and Raman spectra. Intense bands were observed in the IR spectrum at 1889/1848 cm⁻¹, in a region characteristic for Ga–H stretching modes, v(Ga-H), of Ga^{III} species. This value compares to e. g. 1906 cm^{-1} for $[H_2GaOtBu]_2$ ^[39] and 1918 cm⁻¹ for $[H_2GaOC(H)tBu_2]_2$.^[40] The Raman spectrum also features two intense maxima due to the v(Ga-H) modes, differing not in their energies, but in their relative intensities from the IR bands. The ¹H NMR spectrum measured at 233 K (see Figure 4, b) contains a resonance due to the Ga-H protons at 5.4 ppm. Thus there can be no doubt that the new product represents a Ga hydride; finally, the XRD analysis showed the product to be $Ga_3H_5(\mu_3-O)(\mu-tbn)_2$, 4, the tbn analogue of 3. The crystal structure of 4 is displayed in Figure 3 (b). Two of the three possible isomers crystallize together (only one of which is shown in Figure 3, b). Due to the relatively small difference regarding the shape and physical properties between these isomers, they are statistically distributed over all lattice sites of the crystal in an equi-

a)



Figure 4. a) Comparison between the IR (CsI disc) and Raman spectrum (solid material, excited at 514 nm) for compound 4; b) Comparison between the ¹H NMR spectra (200 MHz) for 4 in deuterated dichloromethane and 5 in deuterated toluene solutions.

molar ratio. As anticipated, the molecular structure resembles that of **3**. Figure 5 compares the experimental IR spectrum with a simulation based on quantum chemical (DFT) calculations. It can be seen that the general level of agreement is excellent. The v(CN) mode gives rise to the strongest band in the spectrum, located at 1584 cm⁻¹ in the experimental and 1636 cm⁻¹ in the calculated spectrum. The IR band of this mode is very intense, but the corresponding Raman signal extremely weak.



Figure 5. Comparison between experimental and calculated (B3LYP/6-311++G(d,p)) IR spectrum of 4.

htbo

Finally we studied the reaction between Me₃N-GaH₃ and htbo. In this case, a new product can be isolated also in the absence of H₂O. However, low temperatures (–15 °C) are required, since this product, **5**, already decomposes slowly in solution at room temp. Its IR and Raman spectra are displayed in Figure 6 (a). Both spectra contain a pair of intense absorptions at ca. 1911/1857 cm⁻¹, a region typical for v(Ga–H) modes in Ga^{III} hydrides. For comparison, an intense Raman signal at 1884 cm⁻¹ due to v(Ga–H) was observed for [HClGa(μ -hpp)]₂.^[19] For trimeric methylamidogallane, [H₂GaNHMe]₃, and dimeric *tert*-butylamidogallane, [H₂GaNH*t*Bu]₂, the Raman spectra gave evidence for Ga–H stretching modes at 1897 and 1904/ 1873 cm⁻¹, respectively.^[41]

In the case of [H₂GaNMe₂]₂,^[42] the IR spectra recorded for the vapour phase at 290 K and for the solid at 77 K displayed bands due to the Ga-H stretching modes at 1911/ 1907/1901/1870 and 1885 cm⁻¹, respectively. The experimental spectrum is in excellent agreement with the simulated spectrum for the hydride [H2Ga(µ-tbo)]2 on the basis of quantum chemical calculations (see part b of Figure 6). Raman spectra of solid [H₂GaNMe₂]₂ at 77 K and of C₆H₆ solutions displayed signals at 1890/1875 and 1888 cm⁻¹, respectively. In the ¹H NMR spectrum of 5 recorded at 233 K in perdeuterated toluene (see Figure 4, b), a relatively broad signal at 5.4 ppm can be assigned to the four protons attached to the gallium atoms, finally, we were able to grow crystals of 5. From the XRD analysis in combination with all other data, 5 can be identified unambiguously as the new binuclear gallium hydride $[H_2Ga(\mu-tbo)]_2$. Its crystal



Figure 6. a) Comparison between the IR (CsI disc) and Raman spectrum (solid material, excited at 514 nm) for compound 5<; b) Comparison between experimental and calculated (B3LYP/6-311++G(d,p)) IR spectrum of **5**.

structure is depicted in Figure 7. The unit cell contains two slightly different molecules, which both adopt a boat-type conformation, in difference to the chair-type conformation found in the case of $[HClGa(\mu-hpp)]_2$.^[23] This change from chair- to boat-conformation is not unprecedented in this field. Hence we also found a change from chair- to boattype structure for the pair of molecules $[H_2B(\mu-hpp)]_2/$ $[H_2B(\mu-tbo)]_2$.^[18,22] The two Ga atoms in 5 are separated by 373.9(2)/368.9(3) pm. The Ga-N bond lengths cover the region 187.2(2) (Ga1-N1)-195.5(2) (Ga4-N8) pm. Values in the range 102.50(9)-105.18(9)° were found for the N-Ga-N bonding angles. The structure of 5 can be compared with that of the (pyrazol-1-yl)gallane dimer $[H_2Ga(\mu-pz)]_2$, see Scheme 6,^[43] which also adopts a boat-type conformation (like their boron counterparts ^[44]). This molecule features slightly longer Ga-N distances of 197.1(6)/197.7(8) pm, and smaller N-Ga-N bond angles of 96.5(0.5)/ $97.7(0.4)^{\circ}$ compared with 5. In solution we obtained clean ¹H NMR spectra of **5** only at low temperatures (≤ -20 °C), and observed decomposition with gas evolution at room temp. On the other hand, the solid material turned out to be stable even at 80 °C. Unfortunately we were not able to characterize the decomposition products. However, similar to $[HClGa(\mu-hpp)]_{2}$,^[23] dehydrogenation is likely to occur at the first place, leading to $[HGa(\mu-tbo)]_2$.



Figure 7. Molecular structure of $[(\mu-tbo)_2(GaH_2)_2]$ (5). Vibrational ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, bond angles in deg.): Gal-N1 1.872(2), Gal-N4 1.949(2), Ga2-N2 1.897(2), Ga2-N5 1.9270(19), Ga3-N7 1.925(2), Ga3-N10 1.922(2), Ga4-N8 1.955(2), Ga4-N11 1.875(2), N1-C1 1.301(3), N2-C1 1.328(3), N3-C1 1.331(3), N4-C6 1.322(3), N5-C6 1.313(3), N6-C6 1.375(3), N7-C11 1.315(3), N8-C11 1.320(3), N9-C11 1.373(3), N10-C16 1.327(3), N11-C16 1.296(3), N12-C16 1.340(3), Ga1-Ga2-N5 103.04(9), N7-Ga3-N10 102.50(9), N8-Ga4-N11 103.55(9), N1-C1-N2 134.7(2), N4-C6-N5 133.0(2), N7-C11-N8 133.0(2), N10-C16-N11 134.1(2).



Scheme 6. Structure of the (pyrazol-1-yl)gallane dimer.

Quantum Chemical Calculations

Density-functional theory (DFT) calculations were carried out to obtain more information about the structures and especially the reaction thermodynamics for intramolecular dehydrogenation starting with the three hydrides $[H_2Ga(\mu-hpp)]_2$, $[H_2Ga(\mu-tbn)]_2$ and $[H_2Ga(\mu-tbo)]_2$.

The products, the doubly base-stabilized digallane(4) species $[HGa(\mu-hpp)]_2$, $[HGa(\mu-tbn)]_2$ and $[HGa(\mu-tbo)]_2$, feature Ga-Ga bond lengths of 237.9, 242.6 and 248.3 pm, respectively. Dehydrogenation of [H₂Ga(µ-tbo)]₂ turned out to be very mildly exergonic ($\Delta G^0 = -5 \text{ kJ mol}^{-1}$ at 298 K and 1 bar). This is in sharp contrast to the significantly endergonic dehydrogenation reaction of the corresponding boron compound, which is associated with a ΔG^0 value of +115 kJ mol⁻¹ (see Scheme 7). The boron hydride $[H_2B(\mu$ tbo)]2 indeed is a stable molecule showing no signs of thermal dehydrogenation or other decomposition processes even in boiling toluene or *p*-xylene solutions.^[22] In the case of $[H_2Ga(\mu-tbo)]_2$, the ΔG^0 value lies well within the ideal region for reversibility under mild conditions $(\pm 30 \text{ kJmol}^{-1})$. Therefore it will be the main issue of future research in this field to find catalysts for the quantitative

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and clean dehydrogenation of $[H_2Ga(\mu-tbo)]_2$ to give $[HGa(\mu-tbo)]_2$, and then for the hydrogenation of $[HGa(\mu-tbo)]_2$ tbo)]₂ to regain $[H_2Ga(\mu-tbo)]_2$. We showed already in the case of the boron hydride $[H_2B(\mu-hpp)]_2$ that dehydrogenation can be effectively driven catalytically.^[21] Like in the case of the analogue boron compounds, a correlation exists between the ΔG^0 value for dehydrogenation and the N–C–N bite angle of the guanidinate in the $[H_2Ga(\mu-guanidinate)]_2$ species (see Figure 8, a). Thus the dehydrogenation reactions of the hydrides with hpp or tbn bridges between the Ga atoms are more exergonic (-40 and -35 kJ mol⁻¹, respectively). For all guanidinate bridges, the B compounds exhibit a ΔG^0 value larger than their Ga counterparts. As seen from the plot in Figure 8 (b), the difference between the ΔG^0 values is small in the case of hpp bridges (10 kJ mol⁻¹), becoming larger for the bridges (133 kJ mol⁻¹). This trend reflects the greater flexibility of the Ga-Ga bonds (involving more diffuse orbitals). Whereas optimal prerequisites (comparing the three guanidinates hpp, tbn and tbo) for reversibility are reached for hpp bridges in the case of B compounds, they are reached for tbo bridges in the case of Ga compounds.



Scheme 7. Comparison between dehydrogenation reactions of $[H_2Ga(\mu-tbo)]_2$ and $[H_2B(\mu-tbo)]_2$.

Conclusions

The results presented in this work show, in agreement with previous reports on group 13 guanidinate compounds, that acyclic guanidinates adopt an end-on, κ^2 -type bonding mode, while bicyclic guanidinates prefer bridging bonding modes. The bonding mode can be explained easily by the orientation of the frontier orbitals at the guanidinate nitrogen atoms (see also the comprehensive discussion by Coles^[2b]). Hence the two nitrogen donor orbitals are generally oriented towards the "mouth" of the ligand in the case of acyclic guanidinates (ideal for a chelating bonding mode), but almost coplanar in the bicyclic guanidinate hpp⁻ (supporting a bridging bonding mode). For the purposes outlined in the Introduction of this work, bicyclic guanidinates are therefore more attractive.



Figure 8. a) Calculated ΔG value (at 298 K, 1 bar) for dehydrogenation of [H₂Ga(μ -guanidinate)]₂ to give [HGa(μ -guanidinate)]₂ as a function of the bite angle N–C–N in the bicyclic guanidinate substituent. Guanidinate = hpp, tbn or tbo; b) Comparison between hydrogenation of [HE(μ -guanidinate)]₂ for E = B and E = Ga.

The first synthesis of a stable hydride $[H_2Ga(\mu-guanidin$ ate)]₂ featuring as guanidinates bridging the substituents can be used as basis for future research activities. This hydride slowly decomposes in solution already at room temp., but can be stored in solid form at room temp. without signs of decomposition. Dehydrogenation in the solid state occurs at 80 °C, presumably leading to the doubly basestabilized digallane(4) [HGa(µ-tbo)]₂. According to quantum chemical calculations this dehydrogenation reaction is mildly exergonic at standard conditions (ΔG^0 = -5 kJmol^{-1}). Future research in this field will focus on the catalytic dehydrogenation at low temperatures in solution. We showed already for similar boron hydrides that dehydrogenation can be effectively catalysed by Rh complexes (representing pre-catalysts in a presumably heterogeneous catalysis).[18,22]

Another compound, synthesized herein, which will be used in future synthetic work, is the trinuclear Ga hydride Ga₃H₅(μ_3 -O)(μ -tbn)₂ featuring a central O atom bound to three Ga^{III} atoms in a trigonal planar fashion. Future research will focus on the design of new trigallacycles. The first step in this direction is the synthesis of the monocationic species [{GaH(μ -tbn)}₃(μ_3 -O)]⁺ (see Scheme 8) by reaction of Ga₃H₅(μ_3 -O)(μ -tbn)₂ with [H₂tbn]⁺ salts.



Scheme 8. Possible structure of the trigallacycle [{GaH(μ -tbn)}₃(μ ₃-O)]⁺.

Experimental Section

General: All manipulations were carried out under dry Ar atmosphere using standard Schlenk techniques. The bicyclic guanidines htbo and htbn were prepared as described in the literature.^[36] NMR spectra were measured with a Bruker Avance DPX AC200 or Bruker AVII 400 spectrometer. IR spectra were recorded with a Biorad Excalibur FTS 3000 spectrometer. A Jobin–Yvon T64000 Raman spectrometer was used for Raman measurements. The spectra were excited with the 514 nm line of an Ar⁺ ion laser. Elemental analysis was carried out at the Microanalytical Laboratory of the University of Heidelberg for compounds 4 and 5. Compound 2 turned out to be too unstable, and compound 3 was obtained in small amount as crystalline material suitable for XRD, but no further analysis. EI mass spectra were obtained on a Trinnigan MAT 8230 or a JEOC JMS-700 instrument.

[(iPr)2NC(NCy)2LiOEt2]2: 6.3 mL of nBuLi (10 mmol) was added dropwise to a solution of 1.4 mL of diisopropylamine (10 mmol) in 20 mL of Et₂O at 0 °C. The solution was warmed to room temp. and stirred for 1 h. Then it was cooled to 0 °C and 2.06 g of N,N'dicyclohexylcarbodiimide (10 mmol) were added. The solution was warmed to room temp. and stirred for 2 h. Subsequently it was filtered through a pad of Celite and concentrated to ca. 5 mL and used directly without further analysis in subsequent reactions. Crystals were obtained at -30 °C; yield 940 mg (1.2 mmol, 32%). Crystal data for $C_{46}H_{92}Li_2N_6O_2$: Mr = 775.14, $0.30 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$, a =12.884(3), b = 14.329(3), c = 13.203(3) Å, $\beta = 91.63(3)^{\circ}$, V =2436.5(8) Å³, Z = 2, $d_{calc} = 1.057 \text{ Mg m}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.10 to 30.05°, reflections measd. 13774, indep. 7122, $R_{int} = 0.0504$, final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0550$, $wR_2 = 0.1485$.

Ga₂I₄(µ-O){CyN=C(NHCy)(NiPr₂)}₂: First the "GaI" solution was prepared: to a mixture of 456 mg of elemental gallium (6.5 mmol) and 829 mg of iodine (6.5 mmol), 10 mL of toluene were added, and the mixture ultrasonically treated for 2 h. The guanidinate [(iPr)2NC(NCy)2LiOEt2]2 prepared as described above was dissolved in 5 mL of toluene (using ultrasonic treatment) and added to the "GaI" solution by cannula at room temp. Subsequently the reaction mixture was stirred at 60 °C for a period of 2 h. Then it was cooled to room temp. and stirred overnight. The mixture was filtered through a pad of celite and concentrated to ca. 5 mL. Storage at -30 °C afforded a small amount of colourless crystals suitable for X-ray diffraction, but no further analysis was possible. Mr =1278.08, Crystal data for $C_{38}H_{74}Ga_2I_4N_6O$: $0.25 \times 0.20 \times 0.20$ mm³, orthorhombic, space group Ccca, a = 21.368(4), b = 25.341(5), c = 20.490(4) Å, V = 11095(4) Å³, Z = 8, $d_{\text{calcd.}} = 1.530 \text{ Mg m}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} 1.59 to 30.05°, reflections measd.

15683, indep. 8134, $R_{int} = 0.0317$, final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0385$, $wR_2 = 0.1028$.

[(*i*Pr₂N)C(N*i*Pr)₂GaI]₂ (2): To a mixture of 322 mg of elemental gallium (4.8 mmol) and 604 mg of iodine (4.8 mmol), 10 mL of toluene were added. Ultrasonic treatment for 2 h yielded the "GaI" solution. Then the guanidinate was added to this solution by cannula at -78 °C. Subsequently the mixture was stirred and slowly warmed to room temp. After 24 h it was filtered with a cannula and the solvent was concentrated to ca. 5 mL. Storage at -30 °C afforded colourless crystals suitable for X-ray diffraction; yield 412 mg (0.48 mmol, 20%). The material turned out to be highly air- and moisture-sensitive and no elemental analysis was carried out. ¹H NMR (400 MHz, C₆D₆, 296 K): δ = 3.7 (sept, J = 6.4 Hz, 2 H), 3.23 (sept, J = 6.4 Hz, 2 H), 1.34 (dd, J = 6.4 Hz, 12 H), 1.04 (d, J = 6.4 Hz, 12 H) ppm. ¹³C{¹H} NMR (100.55 MHz, C₆D₆, 296 K): $\delta = 167.38$ (CN₃), 49.34 (CH), 46.71 (CH), 27.07 (CH₃), 25.72 (CH₃), 23.22 (CH₃) ppm. Crystal data for C₂₆H₅₆Ga₂I₂N₆: $Mr = 846.01, 0.50 \times 0.30 \times 0.20 \text{ mm}^3$, monoclinic, space group $P2_1/n, a = 13.981(3), b = 9.3060(19), c = 14.184(3)$ Å, $\beta =$ 103.73(3)°, V = 1792.7(7) Å³, Z = 2, $d_{calc} = 1.567$ Mg m⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 1.84 to 30.12°, reflections measd. 29045, indep. 5236, R_{int} = 0.0622, final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0416$, $wR_2 = 0.1032$.

Ga₃H₅(μ³-O)(μ-hpp)₂ (3): A solution of 8 μL (0.48 mmol) deionised and degassed water in 5 mL of THF was added to a solution of 190 mg of Me₃N·GaH₃ (1.44 mmol) in 5 mL of toluene at -78 °C. The reaction mixture was stirred over 6.5 h. Meanwhile it was warmed to 0 °C. 135 mg of hppH (0.97 mmol) were dissolved in 5 mL of toluene, cooled to -78 °C and added by cannula. After several weeks at -30 °C a small amount of colourless crystals suitable for X-ray diffraction, but no further analysis, were obtained. Crystal data for C₁₄H₂₉Ga₃N₆O: *M*r = 506.59, 0.15×0.10×0.10 mm³, monoclinic, space group *P*2₁/*n*, *a* = 15.478(3), *b* = 9.3320(19), *c* = 15.671(3) Å, *β* = 118.08(3)°, *V* = 1997.1(7) Å³, *Z* = 4, *d*_{calc} = 1.685 Mgm⁻³, Mo-*K*_α radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 100 K, *θ*_{range} 1.52 to 27.46°, reflections measd. 9108, indep. 4566, *R*_{int} = 0.0728, final *R* indices [*I* > 2σ(*I*]: *R*₁ = 0.0472, *wR*₂ = 0.1059.

Ga₃H₅(µ³-O)(µ-tbn)₂ (4): 10 mL of dry toluene were treated with a mixture of 9 µL (0.5 mmol) degassed dist. water in 2 mL of THF. Then the solution was added to 128 mg of solid htbn (1 mmol) at -80 °C. After further addition of 202 mg of solid Me₃N·GaH₃ (2.5 mmol) at -80 °C, the solution was stirred for a period of 5.5 h. During this time the temperature was kept below -20 °C. Then the solution was overlayed with 5 mL of pre-cooled n-hexane. Colourless crystals suitable for X-ray diffraction were grown at -18 °C; yield 71 mg (0.15 mmol, 30%). C12H25Ga3N6O (478.54): calcd. C 30.12, H 5.27, N 17.56; found C 30.55, H 5.33, N 17.33. ¹H NMR (200 MHz, C₆D₆, 303 K): δ = 5.7 (br. s, 4 H), 3.15 (m, 8 H), 2.66 (m, 4 H), 2.48 (m, 4 H), 1.35 (m, 4 H) ppm. IR (KBr): $\tilde{v} = 2934$ (m), 2858 (m), 1889 (s), 1848 (s), 1584 (s), 728 (s) cm⁻¹. MS (EI) $m/z = 477 [M - H]^+, 407.1 [M - GaH_2]^+, 391.1 [M - GaH_2 - O]^+,$ 196.1 [H₃Ga(tbn)]⁺, 124.2[tbn]⁺, 68.9 [Ga]⁺. Crystal data for $C_{12}H_{25}Ga_3N_6O$: Mr = 478.54, 0.30 × 0.30 × 0.26 mm³, monoclinic, space group $P2_1/c$, a = 8.7250(17), b = 26.939(5), c = 8.7600(18)Å, $\beta = 119.22(3)^{\circ}$, V = 1797.0(6) Å³, Z = 4, $d_{calc} = 1.769$ Mg m⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T =100 K, θ_{range} 1.51 to 27.51°, reflections measd. 8235, indep. 4122, $R_{\text{int}} = 0.0273$, final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0427$, $wR_2 = 0.1190$.

 $[H_2Ga(\mu-tbo)]_2$ (5): A solution of 267 mg of Me₃N·GaH₃ (2 mmol) in 10 mL of Et₂O was cooled to -78 °C and added to a suspension of 223 mg of htbo (2 mmol) in 10 mL of Et₂O at -78 °C via can-

nula. The mixture was stirred for a period of 3.5 h and warmed gradually to -15 °C during this period. The resulting suspension was filtered and the product obtained in the form of a white powder. Colourless crystals suitable for X-ray diffraction were obtained from a 1:1 mixture of Et₂O and toluene at -18 °C; yield 184 mg (0.5 mmol, 51%). C₁₀H₂₀Ga₂N₆ (363.76): calcd. C 33.0, H 5.5, N 23.1; found C 34.3, H 5.9, N 23.4. ¹H NMR (200 MHz, C₇D₈, 233 K): δ = 5.42 (s, 4 H), 3.58 (t, J = 7.3 Hz, 8 H), 2.16 (t, J = 7.3 Hz, 8 H) ppm. IR (KBr): $\tilde{v} = 2941$ (m), 2855 (m), 1906 (s), 1857 (s), 1627 (s), 700 (vs), 635 (m) cm⁻¹. MS (LIFDI, toluene): m/z = 362 [{Ga(tbo)H}₂]. Crystal data for C₁₀H₂₀Ga₂N₆: Mr = $363.76, 0.43 \times 0.40 \times 0.40 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a = 15.6340(11), b = 7.6490(15), c = 23.837(5) Å, $\beta = 108.17(3)^{\circ}$, V =2708.4(8) Å³, Z = 8, $d_{\text{calcd.}} = 1.784 \text{ Mgm}^{-3}$, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 1.37$ to 28.50°, reflections measd. 25798, indep. 6807, $R_{int} = 0.0563$, final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0321$, $wR_2 = 0.0811$.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius–Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo- K_{α} radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.^[45] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[46,47] Graphical handling of the structural data during solution and refinement was performed with XPMA.^[48] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

CCDC-777676 (for $[(iPr)_2NC(NCy)_2LiOEt_2]_2$), -777677 (for Ga₂I₄(µ-O){CyN=C(NHCy)(N*i*Pr₂)}₂), -777675 (for **2**), -734722 (for **3**), -777679 (for **4**), and -777678 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Details of the quantum chemical calculations.

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