CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600807

A New Class of Binuclear Gallium Hydrides: Synthesis and Properties of $[\{GaCl(hpp)H\}_2]$ (hpp=1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidate)

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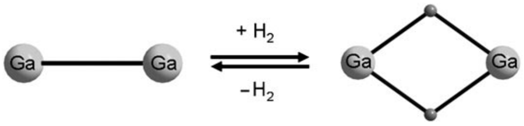
Dedicated to Professor Tony Downs on the occasion of his 70th birthday

Abstract: Herein we report on the synthesis and characterization of the first representative of a new class of gallium hydrides, namely $[\{GaCl(hpp)H\}_2]$ (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidate). Our X-ray diffraction data suggest the presence of weak H–H contacts between adjacent $[\{GaCl(hpp)H\}_2]$ molecules in the crystal. With the aid of quantum-chemical calculations, the pathway of its formation starting with the adduct $H_2ClGa{\cdot}NMe_3$ and the pyrimidine hppH were analyzed. $[\{GaCl(hpp)H\}_2]$ slowly decomposes at 25 °C, a process which presumably leads under H_2 elimination to $[\{GaCl(hpp)\}_2]$. Although we were not yet able to characterize $[\{GaCl(hpp)\}_2]$ experimentally, DFT calculations provide information about its likely structure. According to these calculations, the molecule features a Ga–Ga single bond.

Keywords: reaction mechanisms · gallium · hydrides · quantum-chemical calculations · X-ray diffraction

Introduction

Recently, we have studied the properties and reactivity of ligand-free Ga_2 using the matrix isolation technique.[1] Resonance Raman spectra of Ga_2 allowed an estimation of the bond strength in this diatomic. Interestingly, matrix-isolated Ga_2 reacts at 10 K readily with H_2 to give the cyclic gallium(I) hydride $Ga(\mu\text{-}H)_2Ga$. Thus, the fairly weak Ga–Ga bond and the strong H–H bond are cleaved in favor of Ga–H bonds. This reaction is exothermic by approximately $-100\,kJ\,mol^{-1}$, and opposed to a small barrier of about $30\,kJ\,mol^{-1}$. It is likely that the reaction can be reverted thermally if one can find a means to stabilize Ga_2 and $Ga(\mu\text{-}H)_2Ga$ and prevent them from undergoing further reactions. This, however, is only possible by confining the molecules in small cages of a non-reactive host material. An alternative strategy to follow is the introduction of ligands, which certainly influence the electronic properties to a large extent, but could bring two Ga atoms together in a thermally robust molecule. Therefore, our interest focused on the synthesis of new binuclear Ga hydrides.



There are now several known molecules featuring Ga–Ga bonds. For example, a single bond is present in $[\{GaCl_2(PEt_3)\}_2]$,[2] for which the Ga–Ga bond length was determined to be 242.69(5) pm. Neutral compounds RGaGaR have also been characterized.[3] The molecule $Na_2[Mes_2C_6H_3GaGaC_6H_3Mes_2]$ (Mes = 2,4,6-$iPr_3C_6H_2$), featuring a very short Ga–Ga bond of only 231.9 pm, was first believed to contain a Ga–Ga triple bond.[4] Later analysis has shown that the Na^+ ions are engaged in the bonding.[5]

In other binuclear gallium compounds, the two Ga atoms are bridged by two ligands X such as H, Cl, NR_2, OR, or pyrazolyl derivatives. Among the well-known examples for

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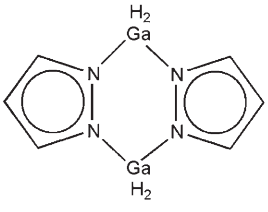
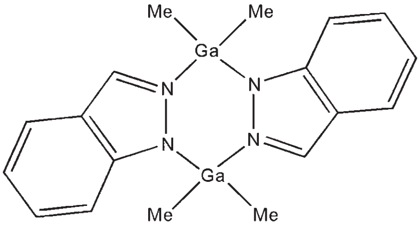
hydrides of the form [{Ga(μ-X)H_2}$_2$] are the D_{2h}-symmetric molecules [{Ga(μ-H)H_2}$_2$],[6] [{Ga(μ-Cl)H_2}$_2$],[7] amido compounds such as [{Ga(μ-NH_2)H_2}$_2$],[8] [{GaH_2(μ-N(H)*t*Bu)}$_2$],[9] [{GaH_2(μ-N(μ-C_2H_4)$_2$CH_2)}$_2$],[10] and hydrazido derivatives like [(H_2Ga{μ-N(H)N(CH_3)$_2$})$_2$][11] as well as alkoxy compounds (e.g. [{GaH_2(μ-O*t*Bu)}$_2$]).[12] Compounds with bridging alkyl groups, for example, [{Ga(μ-C_2H_5)H_2}$_2$],[13] were found to be less stable. In all these examples the two gallium atoms are connected to the same atom of the bridge, and the Ga_2(μ-X)$_2$ center is planar. The Ga···Ga separations in these compounds vary. Thus in [{Ga(μ-H)H_2}$_2$] and [{Ga(Cl)(μ-Cl)H}$_2$], separations of 258.0 and 329.1 pm, respectively, were measured. These values compare with 247–307 pm in the different forms of elemental gallium and twice the covalent radius of tetrahedrally coordinated Ga (252 pm). Although the distance is short in some of these compounds, theoretical calculations argue against significant Ga−Ga interactions.

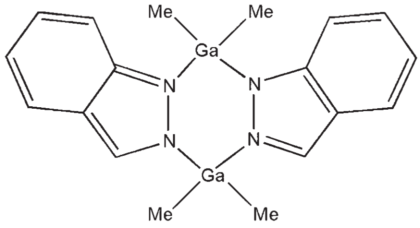
There are other examples in which the two Ga atoms are connected to different atoms of the bridging group. One such example is [{H_2Ga}$_2${μ-N(*t*Bu)CH_2CH_2N(*t*Bu)}].[14] In **1** the two Ga atoms are bridged by a pyrazolyl ligand.[15] In the case of [{(η^1:η^1-ind)(μ-Ga)Me_2}$_2$] (ind = indazolato), both the anti (**2 anti**) and the anti (**2 syn**) form were recently structurally characterized.[16] Crystals of **2 anti** were obtained at −20 °C from toluene, and those of **2 syn** from benzene.



1

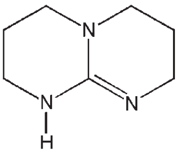


2 anti

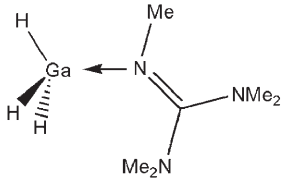


2 syn

The 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidate ion (hpp), the anion of the pyrimidine derivative hppH, **3**, has been used in the past as a promising ligand. For example, several transition metal complexes featuring this ligand have been tested in various catalytic applications.[17] In binuclear complexes of this ligand, two transition metals in formally high oxidation states can be engaged in multiple bonding. Generally, the transition metals are bound to one of the N atoms of each of the hpp ligands, and all metal–nitrogen distances are more or less equal. Of particular interest is the short distance between the two metal atoms in these complexes.[18] Thus, in [Nb_2(hpp)$_4$],[18a] the Nb−Nb bond length is 220.35(9) pm, and in [Ru_2Cl_2(hpp)$_4$],[19] which exhibits two unpaired electrons, a Ru−Ru distance of 232.1 pm was measured. [{Li(hpp)(hppH)}$_2$] is an example for a main group element species containing hpp units.[20] The structure of this species is distinctly different in that the Li atoms form bonds with two N atoms of one hpp ligand, and to one of the N atoms of two other hpp ligands.



3, hppH



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Recently, we have shown that guanidine derivatives form adducts with GaH_3; the resulting products display unusually short Ga−N bonds.[21] In 1,1,3,3-tetramethylguanidine-gallane [{(Me_2N)$_2$CN(H)}GaH_3], **4**, the Ga−N bond length is 198.81(19) pm. This short value is caused by the strong basicity of the guanidine derivative. Here we report on the stabilization of gallium hydrides with the help of the hpp ligand, the anion of a guanidine derivative. In the light of the results available for transition-metal complexes, the ligand might offer the possibility to form binuclear molecules with short Ga−Ga contacts.

Results and Discussion

$H_2ClGa{\cdot}NMe_3$, freshly prepared from NMe_3HCl and Li-GaH_nCl$_{4-n}$, which itself had been made from $GaCl_3$ and LiH, was allowed to react with an excess of hppH in diethyl ether at −20 °C. White crystalline needles suitable for X-ray diffraction analysis precipitated after removal of the majority of the solvent and storage of the remaining oil for about one week at 0 °C. These crystals turned out to consist of [{GaCl(hpp)H}$_2$] molecules. All attempts to obtain crystals of the adduct $H_3Ga{\cdot}$hppH or the hydride [{Ga(hpp)H_2}$_2$] at various temperatures failed. Most likely, [{Ga(hpp)H_2}$_2$] is a liquid (oil) at 0 °C, in contrast to [{GaCl(hpp)H}$_2$], which is solid at this temperature. The preparation was repeated with varying ratios of LiH to optimize the yield of the crystalline product, which in all cases turned out to be [{GaCl(hpp)H}$_2$]. Its treatment with Me_3SiH failed to give another crystalline product.

The structure of $[\{\mathrm{GaCl(hpp)H}\}_2]$, as determined by X-ray diffraction, is shown in Figure 1. The dimeric complex is located on a crystallographic center of inversion. In addition, there is an approximate local mirror plane that relates the two $C_7H_{12}N_3$ ligands, resulting in a local point symmetry approximating to $2/m$ (C_{2h}). The two CN_3 groups are exactly parallel and almost coplanar, with one Ga atom lying above the plane and one below. The N-Ga-N angle is not 180°, like in transition-metal complexes such as $[\mathrm{Nb_2(hpp)_4}]$,[18b] but 110.1(2)°, a value close to the ideal tetrahedral angle. The other angles at the Ga atoms are also close to this value. This geometry suggests that the molecule can be regarded in an extreme description as two $[\mathrm{GaX_4}]^-$ units which are linked together through positively charged bridging $[\mathrm{hpp}]^+$ ligands. There are nine possible resonance structures for such a molecule (see Figure 2 for four of them), implying that the positive partial charge on each of the hpp ligands is distributed over three atoms. Thus, following this extreme description, the positively charged bridging hpp ligands stabilize two $[\mathrm{GaX_4}]^-$ units in close geometric proximity to each other, with Ga···Ga separations of not more than 330.69(10) pm. The Ga–H and Ga–Cl distances are 147(5) and 220.15(15) pm, respectively. For comparison, in $\mathrm{Ga^+[GaHCl_3]^-}$, the Ga–H and Ga–Cl distances are 132(6) and 219.85(9)/221.2(1)/221.99(8) pm, respectively.[22] It is well known that the experimentally determined Ga–H bond lengths vary to quite a large extent from compound to compound, presumably also because of problems with its determination from Fourier difference maps. In $[(\mathrm{GaH_2\{N(\mu\text{-}C_2H_4)_2CH_2\}})_2]$, values of 155(3)/156(3) pm were measured for the Ga–H distances and according to the Cambridge database, the average Ga–H distances are 151(11) pm,[10b] which is in pleasing agreement with the value obtained for $[\{\mathrm{GaCl(hpp)H}\}_2]$. We also calculated the structure of this molecule by applying DFT methods [BP86/SV(P)]. In Table 1 and Table 2, the experimentally determined bond lengths and angles are compared to the calculated ones. It can be seen that the general level of agreement is quite good, although the calculated Ga–H bond length is by as much as 10 pm longer than the experimentally determined value. Most likely, the experimental value comes out too short.

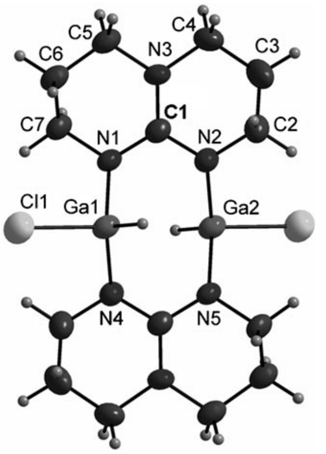

Figure 1. Molecular structure of $[\{\mathrm{GaCl(hpp)H}\}_2]$ as determined by X-ray diffraction.

Table 1. Comparison between the experimentally determined and calculated bond lengths [pm] for $[\{\mathrm{GaCl(hpp)H}\}_2]$.

Bond length	Exptl	Calcd[a]
Ga1–Cl1	220.15(15)	225.1
Ga1–N1	194.2(4)	199.0
Ga1–N4	192.8(4)	199.0
Ga1–H1	147(5)	157.5
N1–C1	135.3(6)	135.4
N1–C7	146.8(6)	146.5
C1–N2	134.7(6)	135.3
C1–N3	133.5(6)	137.6
N2–C2	147.8(7)	146.5
C2–C3	151.1(10)	153.1
C3–C4	150.7(8)	152.9
C4–N3	148.3(6)	146.9
N3–C5	147.3(6)	146.9
C5–C6	152.0(7)	152.9
C6–C7	151.2(7)	153.1

[a] BP86/SV(P) calculations.

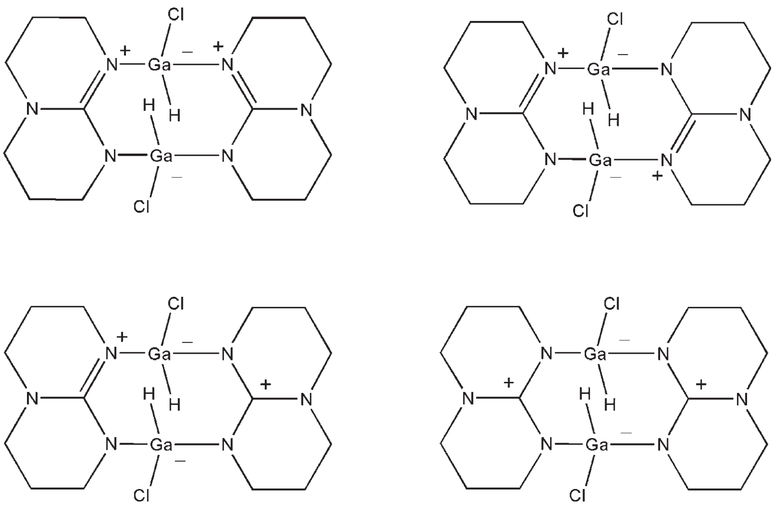

Figure 2. Four of the nine resonance structures that can be drawn for $[\{\mathrm{GaCl(hpp)H}\}_2]$.

The packing of the molecular units in the crystal is shown in Figure 3. In the case of $[\mathrm{H_3Ga\{N(H)C(NMe_2)_2\}}]$, H–H contacts of 210(5) pm were found between the negatively polarized hydrogen atom attached to the Ga center and

Table 2. Comparison between the experimentally determined and calculated bond angles [°] for [{GaCl(hpp)H}$_2$].

Bond angle	Exptl	Calcd[a]
Cl1-Ga1-N1	104.20(12)	102.3
Cl1-Ga1-N4	104.22(13)	102.3
N1-Ga1-N2	110.1(2)	110.3
Cl1-Ga1-H1	106.2(19)	113.8
N1-Ga1-H1	113.8(19)	113.5
N2-Ga1-H1	117.0(20)	113.6
Ga1-N1-C1	115.5(3)	117.3
Ga1-N1-C7	122.1(3)	117.4
C1-N1-C7	115.2(4)	117.0
N1-C1-N2	117.3(4)	118.5
N1-C1-N3	120.8(4)	120.7
N2-C1-N3	121.9(4)	120.8
Ga2-N2-C1	119.2(3)	117.4
Ga2-N2-C2	122.4(3)	121.0
C1-N2-C2	115.3(4)	117.0
N2-C2-C3	108.5(5)	109.3
C2-C3-C4	108.8(5)	108.8
C3-C4-N3	111.6(4)	112.9
C1-N3-C4	123.3(4)	123.2
C1-N3-C5	124.4(4)	123.2
C4-N3-C5	112.2(4)	113.6
N3-C5-C6	111.8(4)	112.9
C5-C6-C7	108.6(4)	108.8
N1-C7-C6	109.2(4)	109.3

[a] BP86/SV(P) calculations.

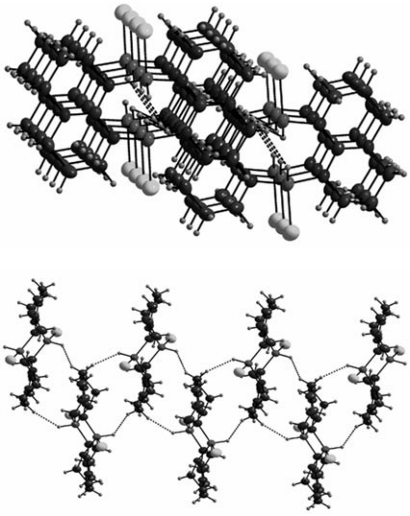

Figure 3. The packing arrangement of the [{GaCl(hpp)H}$_2$] molecules in the crystal.

the positively polarized hydrogen atom attached to the N atoms. The closest distance between H atoms of adjacent molecules in crystals of [{GaCl(hpp)H}$_2$] are 231(5) and 237(4) pm, which are the distances between the H atoms attached to the Ga center, and the H atoms of one of the CH$_2$ groups of the hpp ligands. Although these contacts are significantly longer than those in [H$_3$Ga{N(H)C(NMe$_2$)$_2$}] (210(5) pm),[21] they are still within the range of 200–240 pm prescribed for unconventional dihydrogen bonding of this type.[23] Moreover, we have already mentioned that the Ga–H bond lengths are in reality presumably slightly longer than the measured value of 147(5) pm. This would imply that the intermolecular H–H contacts are in reality shorter than the measured values of 231(5) and 237(4) pm. Detailed quantum-chemical calculations are in progress to analyze the strength of these interactions.

The compound was further characterized by Raman spectroscopy. The Raman spectrum recorded from one of the crystals is shown in Figure 4. A strong and sharp signal at 1884 cm^{-1} can immediately be assigned to the in-phase ν(Ga–H) mode. The position is on the low wavenumber side of the region in which Ga–H stretches of comparable compounds are expected to show (e.g. [{Ga(μ-Cl)H$_2$}$_2$] 2020/1990/1985,[24] [{Ga(Cl)(μ-Cl)H}$_2$] 2047/2051,[25] Ga$^+$[GaCl$_3$H]$^-$ 1960,[22] [(GaH$_2${N(H)N(CH$_3$)$_2$})$_2$] 1912/1897 cm^{-1}). The low frequency is caused by the relatively high electron density on the Ga atoms for which the bridging hpp ligands can be made responsible. That the wavenumber of Ga–H stretches are highly sensitive to changes of the electron density on the Ga metal, also becomes evident from the comparison between the wavenumbers measured or calculated for the Ga–H stretches in H$_2$ClGa and H$_2$ClGaNMe$_3$. In this case the wavenumber of the symmetric GaH$_2$ stretch decreases from 1945.4 cm^{-1} in H$_2$ClGa to 1897.1 cm^{-1} in H$_2$ClGaNMe$_3$ (according to BP/SVP calculations). Owing to the presence of heavy mode coupling, the other signals are less easy to assign. A weaker signal at 332 cm^{-1} comes in a region typical for Ga–Cl stretches of terminal Ga–Cl bonds in Ga^{III} compounds. For example, in Ga$^+$[GaCl$_3$H]$^-$, the symmetric Ga–Cl stretch occurs at 350 cm^{-1}, and the antisymmetric one occurs at 321 cm^{-1}. The doublet feature at 1464/1444 cm^{-1} fits for the CH$_2$ scissor mode, and the two sharp signals at 991 and 817 cm^{-1} most likely arise from C–C and C–N stretches. The C–H stretching region shows at least six signals (at 3013, 2981, 2936, 2912, 2859 and 2795 cm^{-1}). Possibly, the intermolecular H–H contacts in the crystal lead to a red-shift of some of the stretches. Table 3 compares the experimentally observed wavenumbers with the ones calculated at the BP/SV(P) level of theory for modes involving motion of the Ga atoms.

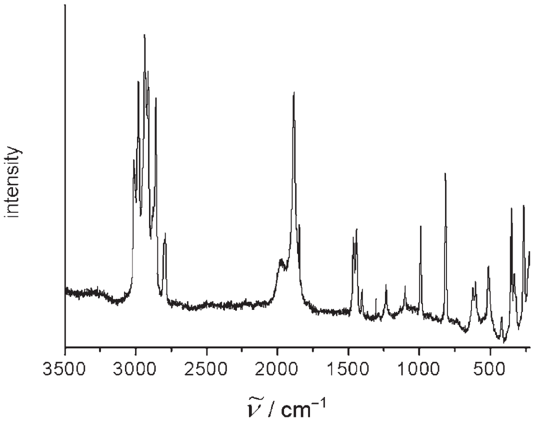

Figure 4. Raman spectrum of [{GaCl(hpp)H}$_2$].

Table 3. Comparison between some of the experimentally observed and calculated [BP86/SV(P)] wavenumbers (in cm^{-1}) for modes of [{GaCl(hpp)H}$_2$] involving motions of the Ga atoms and their approximate description.

Obs.	Calcd	Description of molecular motion (symmetry)
[a]	1939.0	antisymmetric Ga–H stretch (a_u)
1884	1937.4	symmetric Ga–H stretch (a_g)
[a]	619.8	out-of-plane[b] Ga–H bending mode (a_u)
625	598.5	out-of-plane[b] Ga–H bending mode (a_g)
[a]	564.0	in-plane[b] Ga–H bending mode (a_u)
604	562.6	in-plane[b] Ga–H bending mode (a_g)
332	342.9	symmetric Ga–Cl stretch (a_g)
[a]	335.7	antisymmetric Ga–Cl stretch (a_u)

[a] Raman silent. [b] Plane defined by the two Ga–H bonds.

The extremely small energy difference between the symmetric and antisymmetric Ga–H stretches is consistent with very weak coupling between the two Ga–H oscillators through the hpp bridges.

The most likely intermediate on the way to [{GaCl(hpp)H}$_2$] formation is the adduct $H_2ClGa \cdot hppH$, which then loses dihydrogen to form the product. The obvious question which arises is why the experiments give no hint of this complex. DFT calculations (BP/SVP), which were carried to find an answer to this question, revealed that $H_2ClGa \cdot hppH$ can adopt two structures (see **A** and **B** in Figure 5). The H–H contact in structure **B** is 175.8 pm, a value which is extremely short for H–H bonding of this sort. It should also be mentioned that form **B** is chiral. Structure **A** features a Cl–H contact of 211.7 pm. For comparison, in the compounds [MCl$_2$(hpp)$_2$] (M = Mn, Fe, Co, or Ni), intramolecular H–Cl distances of 246, 252, 257, 245, and 247 pm were found.[26] According to the calculations there seems to be a small preference for structure **A**. However, the energy difference between **A** and **B** is not more than 7 kJ mol^{-1}. Thus, in solution an equilibrium should exist between both forms. Form **A** is further characterized by Ga–H, Ga–Cl, and Ga–N bond lengths of 158.7/159.0, 229.2, and 204.4 pm, respectively. Thus, the Ga–N bond length is slightly longer than in [H$_3$Ga{N(H)C(NMe$_2$)$_2$}] (198.81(19) pm).[21] The N–H bond length increases slightly from 102.3 in uncoordinated hppH to 104.4 pm in the adduct.

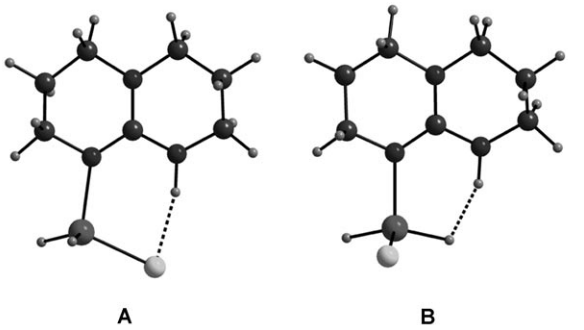

Figure 5. Possible structures of $H_2ClGa(hppH)$, featuring either intramolecular H–Cl (structure **A**) or H–H (structure **B**) contacts.

The formation of adduct **A** is predicted to be exothermic by −66 kJ mol^{-1}. The reaction of two moieties of **A** to give, besides H_2, the identified and characterized end-product [{GaCl(hpp)H}$_2$] is calculated to be exothermic by −44 kJ mol^{-1}. Because both reactions are exothermic and the barrier for H_2 elimination from $H_2ClGa \cdot hppH$ is likely to be small due to the already established H–H contacts, the reaction does not stop at the stage of the adduct but proceeds to give [{GaCl(hpp)H}$_2$]. The complete reaction pathway is illustrated in Figure 6.

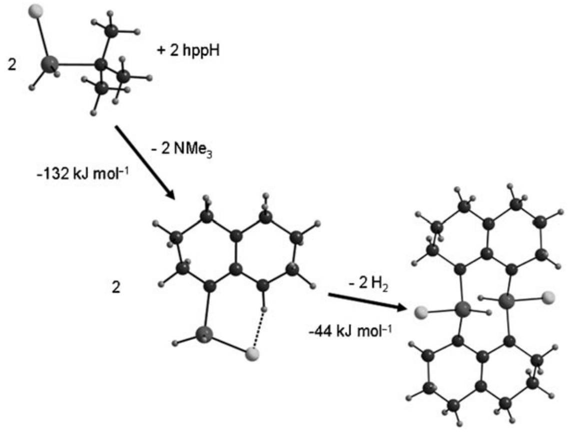

Figure 6. Structures and relative energies of the authenticated and possible products of the reaction between $H_2ClGa \cdot NH_3$ and hppH.

To test the thermal stability of [{GaCl(hpp)H}$_2$], the compound was gently heated. At about 10 °C, it melted to form a colorless liquid. Once the temperature reached about 22 °C, bubbles started to evolve. The compound was kept at 28 °C for 15 minutes during which time gas (presumably dihydrogen) was released. A slightly oily residue was left at the end. This residue can be dissolved in diethyl ether. Unfortunately, we were, despite several attempts, so far not able to characterize this oil in more detail. Our quantum-chemical calculations suggest that the most likely (first) product of this decomposition is [{GaCl(hpp)}$_2$]. Indeed, mass spectra recorded for the compound reveal evidence for the M^+ peaks and several signals assignable to fragments of this species. Thus one of the strongest group of signals can be assigned to the monomer [ClGa(hpp)]$^+$. Figure 7 compares the observed and simulated patterns for this fragment. It can be seen that the agreement is excellent, if one assumes that some smaller peaks in this region arise from this species after loss of one or even two H atoms. Although we were so far not able to characterize [{GaCl(hpp)}$_2$] in our experiments, quantum-chemical calculations provide some insights into its possible structure and the energy of its formation. Figure 8 illustrates the calculated structure.

It can be seen that [{GaCl(hpp)}$_2$] contains a Ga–Ga bond (235.3 pm).[27] The Cl-Ga-Ga-Cl unit adopts a *cis*-bent arrangement with Cl-Ga-Ga bond angles of 154–156°. The

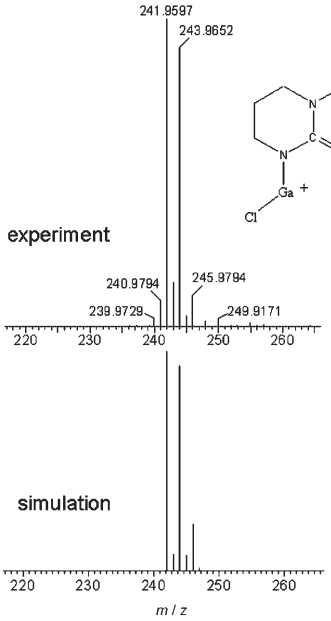

Figure 7. Part of the mass spectrum (experimental and simulated) for [{GaCl(hpp)H}$_2$] showing the peaks due to the fragment [ClGa(hpp)]$^+$.

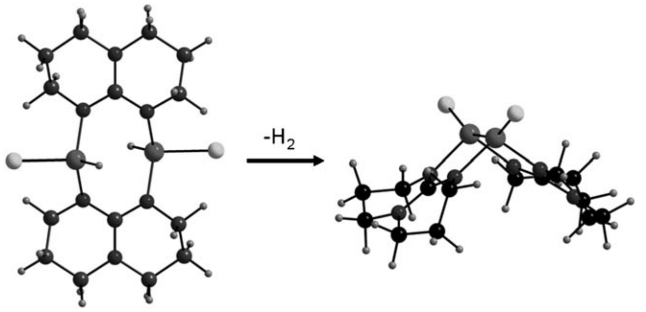

Figure 8. Possible product of the thermal decomposition of [{GaCl(hpp)H}$_2$].

Ga–N bond lengths (201.7 pm) are slightly longer than in [{GaCl(hpp)H}$_2$] molecule (calculated value 199.0 pm). The N-Ga-N angle and the Ga–Cl bond length measure 103/106° and 221.0–221.7 pm, respectively. The decomposition was calculated to be slightly endothermic (energy change of +28 kJ mol^{-1}). Decomposition is favored kinetically by the high volatility of the H$_2$ molecule.

Conclusion

[{GaCl(hpp)H}$_2$] is the first representative of a new class of compounds bearing the general formula [{MX$_2$(hpp)}$_2$] (with M being a Group 13 element and X being hydrogen, halogen, or alkyl). According to calculations, the precursor to this binuclear species, the adduct H$_2$ClGa·hppH, features short Cl–H or H–H contacts. The latter are responsible for the facile H$_2$ elimination. In [{GaCl(hpp)H}$_2$], the Ga atoms are tetrahedrally coordinated, and the compound can roughly be described as two [GaX$_4$]$^-$ units which are kept in close proximity to each other with the aid of two bridging hpp$^+$ ligands. Thermal decomposition of [{GaCl(hpp)H}$_2$] presumably leads, under further H$_2$ elimination, to [{GaCl(hpp)}$_2$], featuring a Ga–Ga single bond. Since [GaX$_4$]$^-$ is formally valence isoelectronic to CH$_4$, this decomposition reaction can be compared to the reaction of two CH$_4$ molecules to give C$_2$H$_6$ and H$_2$. We are currently extending our work to other guanidine derivatives and also to Al compounds, which might prove to be interesting for catalytic applications.

Experimental Section

Preparation of [{GaCl(hpp)H}$_2$]: An excess of Me$_3$N·HCl (2.0 g, 21 mmol) was transferred to a Schlenk tube connected to the Schlenk line and cooled to −78 °C using a solid CO$_2$/acetone bath. At this temperature, diethyl ether (~10 mL) was added. Previously prepared LiGaH$_n$Cl$_{4-n}$ in diethyl ether at −78 °C was then transferred by cannula to the reaction vessel. The solution was then allowed to warm up to 0 °C and stirred at this temperature for four hours. With an 80 % yield assumed so far in the reaction, 1.11 g (8 mmol) of the solid hppH was transferred in the glove box to a Schlenk reaction vessel. After connection to the Schlenk line, the vessel was cooled to −78 °C and the hppH was dissolved in diethyl ether (ca. 10 mL). Then the H$_3$Ga·NMe$_3$ was added in at −78 °C. The reaction mixture was allowed to warm up to −20 °C and stirred at this temperature for two hours. After completion of the reaction, the final product was split into two bulbs, one of which had half of its solvent pumped away and was stored in a refrigerator at −78 °C. The other bulb had all bar about 5 mL of the solvent pumped away and was stored in a refrigerator at 0 °C. After about one week, crystals were found to have grown in the bulb held at 0 °C. The yield for this reaction is difficult to estimate because it proved impossible to completely isolate the product. When the crystals grew, they were left in an oily residue. The crystals started to melt at about 10 °C. For X-ray diffraction analysis, a single crystal of [{GaCl(hpp)H}$_2$] having dimensions of approximately 0.04 × 0.04 × 0.18 mm was mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N$_2$ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured by using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Intensity data were processed by using the DENZO-SMN package.[28] Examination of the systematic absences of the intensity data showed the space group to be $P2_1/n$. The structure was solved by using the direct-methods program SIR92,[29] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[30] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The hydride hydrogen atom was located in a difference Fourier map, and its coordinates and isotropic thermal parameters subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0691$, $wR = 0.0683$. CCDC-617332 contains 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.

Raman spectra were recorded on a Jobin Yvon Labram spectrometer equipped with a microscope, through a tenfold magnification objective (Olympus), by accumulating four scans. A 40-mW argon-ion laser (514 nm) was used to excite the spectra. The 1800 L mm^{-1} grating provided a resolution starting from 1.5 cm^{-1} at 200 cm^{-1} up to 1.0 cm^{-1} at 3600 cm^{-1}. The abscissa was calibrated with the 520.7 cm^{-1} peak of a silicon standard. Detected Raman signals (in cm^{-1}) for [{GaCl(hpp)H}$_2$]: 3013, 2981, 2936, 2912, 2859, 2795, 1884, 1465, 1443, 1403, 1235, 1102, 991, 817, 625, 604, 513, 420, 350, 332, 264, 226. Mass spectra were obtained by using a Micromass GCTof spectrometer with a temperatureprogrammed solid probe inlet using electron impact ionization. Signals due to the following fragments were identified: $[Ga]^+$, $[C_4H_6N_2]^+$, $[C_4H_6N_3]^+$, $[GaCl]^+$, $[C_5H_8N_3]^+$, $[C_6H_{10}N_3]^+$, $[C_7H_{12}N_3]^+$, $[GaClC_7H_{12}N_3]^+$, $[Ga_2Cl_2C_{14}H_{24}N_6]^+$. Elemental analysis (%) calcd for $[\{GaCl(hpp)H\}_2]$: C 31.0, H 5.6, N 18.1, Cl 15.3, Ga 30.0; found: C 36.6, H 6.3, N 17.8, Cl 15.0, Ga 24.2. Deviations between observed and expected percentages might be caused by partial decomposition of the sample which was kept at room temperature prior to the measurement and the presence of traces of other products (with less and/or more Cl atoms).

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie for their continuous financial support.

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Received: June 9, 2006