An Intramolecularly Base-Stabilized Gallium Dihydride. A Link between Organometallic and Aqueous Gallium Chemistry

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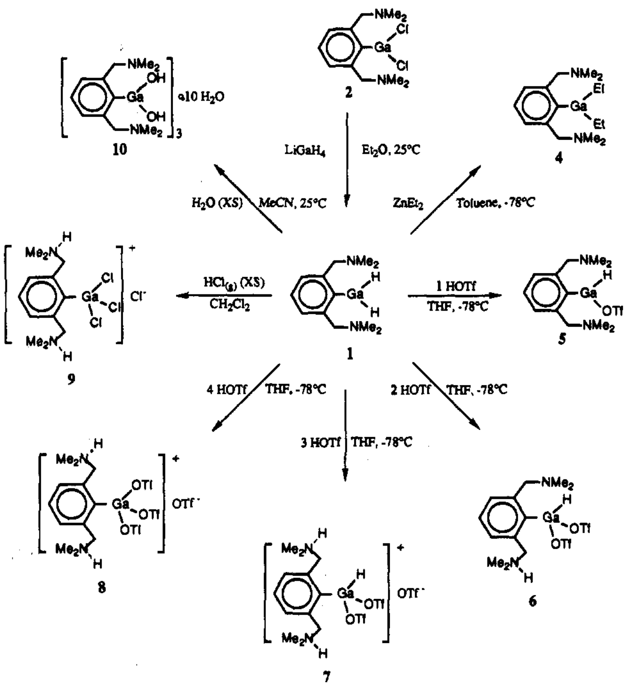
Gallium hydride entities have been detected on surfaces during chemical vapor deposition from organogallium sources[1] and by dissociative adsorption of gallane adducts on oxidized silicon surfaces.[2] However, very little is known about the structural and chemical properties of neutral molecules featuring Ga–H bonds.[3] Indeed, it was only in 1991 that digallane, the elusive binary hydride of gallium, was synthesized and characterized definitively.[4] Other examples of structurally authenticated (electron diffraction) compounds with GaH_x moities are confined to the dinuclear species $[Me_2Ga(\mu\text{-}H)]_2$,[5] $[H_2Ga(\mu\text{-}X)]_2$ (X = Cl,[6] Me_2N[7]), and $[H_2Ga(\mu\text{-}H)_2BH_2]$[8] and the novel monomer $[HGa(BH_4)_2]$ with a pentacoordinate gallium atom.[9] We were particularly interested in developing a thermally stable organometallic compound with a terminal GaH_2 group in order to learn about the reactivity patterns of this functionality. In view of the fact that $GaMeH_2{\cdot}NMe_3$ undergoes rapid scrambling reactions at ambient temperature,[10] we opted to enhance the stability of the target molecule by means of intramolecular Lewis base stabilization. Herein we describe (i) the first stable organometallic gallium dihydride, (ii) a preliminary study of its unusual reaction chemistry, and (iii) the first bis(hydroxide) of gallium.

Gallium dihydride **1** was prepared via the reaction of the corresponding gallium dichloride **2**[11] with $LiGaH_4$. Interestingly, the reaction of **2** with $LiAlH_4$ results in transmetalation and formation of the corresponding aluminum dihydride **3**.[12] Moreover, treatment of the indium analogue of **2**[13] with $LiGaH_4$ produces **1**. The NMR data for **1**[14] are in accord with the structure proposed in Scheme 1. Particularly important are the terminal hydride ^1H resonances which appear as a broad singlet at δ 4.60 ($w_{1/2}$ = 21 Hz). Further conformation of the presence of the GaH_2 moiety was provided by the IR spectrum of **1**, which exhibits Ga-H stretching frequencies at 1837 and 1854 cm^{-1}. An X-ray analysis[15] reveals that **1** is monomeric in the solid state (Figure 1) and that there are no unusually short intermolecular contacts. The coordination sphere of gallium comprises a distorted trigonal bipyramid in which the axial sites are occupied by two nitrogen atoms and the equatorial sites by the aryl carbon and two hydride ligands. The hydride ligands were detected in the final difference map.

Scheme 1



Compound **1** is remarkably stable and survives attempted photolysis (254-nm light, Et_2O solution) and vapor-phase heating (350 °C). Nevertheless, **1** exhibits a diverse reactivity. Thus, reaction with $ZnEt_2$ converts **1** quantitatively into the diethyl analogue $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaEt_2$ (**4**), which was characterized by NMR and mass spectrometry.[14] Previous Ga-H to Ga-alkyl transformations have been effected by olefin hydrogallation rather than by alkyl/hydride exchange.[16] The white zinc-containing product had properties similar to those described for ZnH_2.[17] The hydride reactivity of **1** was explored further by treatment with four successive equivalents of triflic acid (Scheme 1). Interestingly, the first equivalent of HOTf attacks a Ga-H bond to produce **5** in preference to quaternizing a Me_2N group.

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(14) Spectroscopic data are available as supplementary material.

(15) Crystal structure data for **1**: $C_{12}H_{21}GaN_2$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.017(1)$ Å, $b = 17.237(2)$ Å, $c = 9.644(2)$ Å, $\beta = 109.74(1)°$, $V = 1411.0(4)$ Å^3, $\rho_{calcd} = 1.238$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, $\mu = 1.925$ mm^{-1}; 1638 unique data collected ($\theta - 2\theta$ scan technique, $3.5 \leq 2\theta \leq 44.2°$), of which 1171 had $I > 4\sigma(I)$ and were used for structure solution and refinement; $R = 5.35\%$. Crystal structure data for **7**: $C_{15}H_{22}F_9GaN_2O_9S_3$, orthorhombic, space group $Pbcn$, $Z = 8$, $a = 21.306(2)$ Å, $b = 15.175(2)$ Å, $c = 17.540(2)$ Å, $V = 5670.8(8)$ Å^3, $\rho_{calcd} = 1.666$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, $\mu = 1.295$ mm^{-1}; 2832 unique data collected ($\theta - 2\theta$ scan technique, $3.5 \leq 2\theta \leq 41.2°$), of which 1682 had $I > 2\sigma(I)$ and were used for structure solution and refinement; $R = 7.95\%$. Crystal structure data for **9**: $C_{12}H_{21}Cl_4GaN_2$, monoclinic, space group $C2/c$, $Z = 8$, $a = 15.200(3)$ Å, $b = 12.563(3)$ Å, $c = 19.819(4)$ Å, $\beta = 100.79(3)°$, $V = 3717.7(14)$ Å^3, $\rho_{calcd} = 1.447$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, $\mu = 2.045$ mm^{-1}; 3679 unique data collected ($\theta - 2\theta$ scan technique, $3.5 \leq 2\theta \leq 45°$), of which 1338 had $I > 4\sigma(I)$ and were used for structure solution and refinement; $R = 3.35\%$. Details of this structure will be published elsewhere. Crystal structure data for **10**: $(C_{12}H_{21}GaN_2O_2)_3{\cdot}10\,H_2O$, monoclinic, space group $C2/c$, $Z = 8$, $a = 12.443(4)$ Å, $b = 21.212(6)$ Å, $c = 38.970(11)$ Å, $\beta = 95.76(2)°$, $V = 10\,234(5)$ Å^3, $\rho_{calcd} = 1.38$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, $\mu = 1.626$ mm^{-1}; 7759 unique data collected (ω scan technique, $4 \leq 2\theta \leq 45°$), of which 4993 had $I > 4\sigma(I)$ and were used for structure solution and refinement; $R = 5.96\%$.

(16) See, for example, ref 4.

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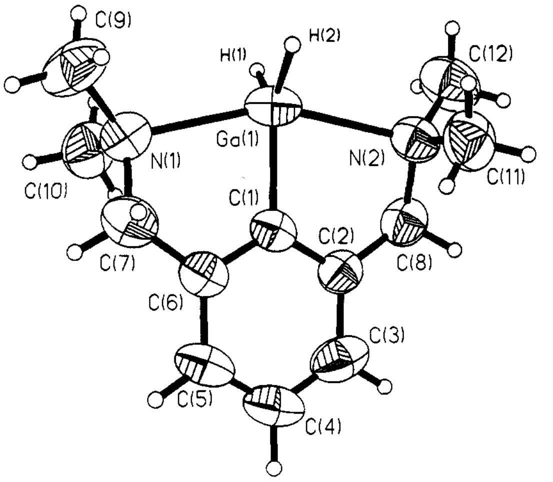

Figure 1. Structure of **1** in the crystal. Selected bond distances (Å) and bond angles (deg): Ga1–N1 2.380(6), Ga1–N2 2.398(6), Ga1–C1 1.968(7), N1–Ga1–N2 155.4(2), C1–Ga1–N1 78.1(2), C1–Ga1–N2 77.4(2).

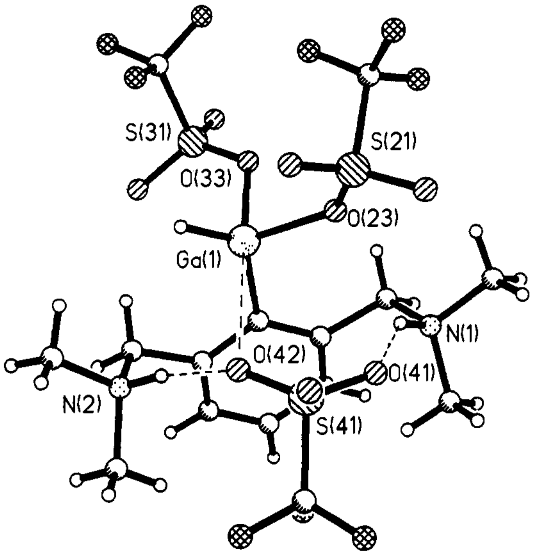

Figure 2. Structure of **7** in the crystal. Selected bond distances (Å) and bond angles (deg): Ga1–H1A 1.42(4), Ga1–C1 1.945(13), Ga1–O23 1.939(8), Ga1–O33 1.962(9), Ga1–O42 3.165(11), C1–Ga1–H1A 125.4(30), C1–Ga1–O23 110.9(5), C1–Ga1–O33 105.5(5), C1–Ga1–O42 80.6(4), O42–Ga1–O33 173.8(4), O42–Ga1–O23 85.3(3), O42–Ga1–H1A 74.4(28), O23–Ga1–H1A 114.2(28).

As a result of the introduction of an electron-withdrawing substituent into the coordination sphere, the hydridic character of the remaining Ga-H bond is severely reduced, a conclusion which is consistent with the downfield shift of the Ga-H resonance. Accordingly, the second equivalent of HOTf quaternizes one of the Me_2N groups, leaving the Ga-H bond intact (compound **6**). Likewise, the third equivalent of HOTf quaternizes the remaining Me_2N moiety to form **7**. It is, in fact, only the fourth equivalent of HOTf that protonates the final Ga-H bond and affords **8**. However, the conversion of **7** to **8** is slow, and isolation of the latter is complicated by acid-catalyzed polymerization of the solvent. However, the reaction of **1** with an excess of HCl proceeds rapidly to afford **9**, which is the tetrachloro analogue of **8**. Each of the products **5**, **6**, **7**, and **9** was isolated and characterized by NMR, mass spectroscopy, and IR.[14] Crystals of compounds **7** and **9** were suitable for X-ray analysis.[15] The structure of **7** (Figure 2) is particularly interesting because the external OTf^- anion is hydrogen-bonded to two NH^+ groups. Moreover, one of the triflate oxygen atoms, O(42), is close to Ga(1) (3.166 Å). This interaction results in an approximately trigonal bipyramidal geometry at gallium and thereby increases the magnitude of the formal negative charge at this center. Hydrogen bonding is also observed in the solid state of **9**. However, in this case, the H–anion–H interaction is intermolecular and serves to link dimeric units together.

Finally, aqueous hydrolysis of **1** affords **10**, the first example of a bis(hydroxide) of gallium. Compound **10** was characterized on the basis of spectroscopic data[14] and by X-ray analysis.[15] The solid state of **10** (Figure 3) consists of an extensively hydrogen-bonded network which features layers of gallium bis(hydroxide) complexes sandwiching a layer of water molecules. As a consequence of the participation in the hydrogen bonding, the $Ga(OH)_2$ moieties point toward the water layers while the hydrophobic aromatic rings are directed away. Hydrogen bonding is also responsible for the cohesion of the gallium-containing organometallic layers since half of the GaOH groups interact directly with GaOH groups from neighboring molecules. To our knowledge, no previous structural data are available for terminal GaOH groups. However, as expected, the average Ga–O distance in **10** (1.824(8) Å) is shorter than those in the bridged hydroxides $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$ (1.957(5) Å)[18] and $[Me_2Ga(\mu\text{-}OH)]_4$ (1.94–1.99 Å).[19]

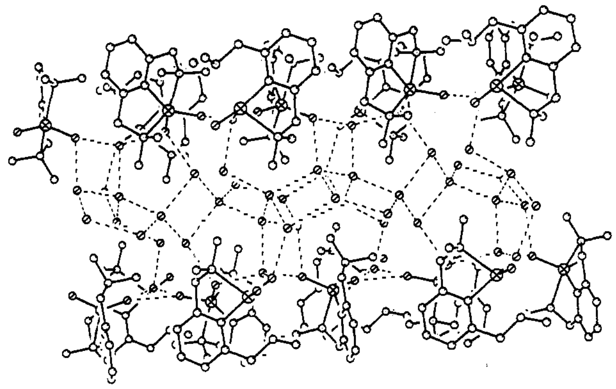

Figure 3. Unit cell packing diagram for **10**. The unit cell consists of two gallium-containing layers sandwiching a water layer. One hydroxyl group of each Ga complex is hydrogen-bonded to the water layer, and the other is hydrogen-bonded to a hydroxyl group of a neighboring Ga complex. The result is a layered packing with the hydrophilic Ga–O groups directed toward the water layer and the hydrophobic phenyl ring and one dimethylamine moiety directed away.

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Supplementary Material Available: Experimental procedure, ^1H NMR, ^{13}C NMR, IR, and MS data for **1**, **4**, **5**, **6**, **7**, **9**, and **10**; tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **1**, **7**, and **10** (27 pages); listings of observed and calculated structure factors for **1**, **7**, and **10** (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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