

Dehydrogenative Ga–Ga Coupling and Hydrogallation in Gallium Hydride Complexes of 3,5-Dimethylpyridine

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Summary: The 2:1 complex of 3,5-dimethylpyridine (L') and dichlorogallane, $(L')_2GaHCl_2$, undergoes dehydrogenative Ga–Ga coupling in boiling toluene to give high yields of $(L')Cl_2Ga-GaCl_2(L')$. The structure of the dinuclear product (which has C_{2h} symmetry) has been determined [$Ga-Ga'$ 2.4000(8) Å]. By contrast, the 1:1 complex of L' and gallium trihydride, $(L')GaH_3$, on prolonged standing at 20 °C or when treated with excess ligand L' , is converted into the hydrogallation product, $(L')(L'H)GaH_2$. In this product, the gallium atom is attached to a pyridine donor ligand L' and a 4-hydro-pyridyl substituent, as proven by a crystal structure determination and by NMR and IR spectral studies. The Ga–N bond length is very significantly shorter for the hydro-pyridyl as compared to the pyridine group, and the carbon atom C^4 of the former has become the center of an aliphatic CH_2 group with its 1H and ^{13}C resonances shifted into the corresponding upfield regions. The C^3-C^4 and C^4-C^5 linkages have been converted into single bonds, with double bonds localized at C^2-C^3 and C^5-C^6 of the $(L'H)$ heterocycle. While the $N-Ga-N$ angle is very small at only 103(1)°, the $H-Ga-H$ angle is exceedingly large at 127(2)°, indicating a strong steric pressure of the seemingly small hydride ligands and that hydride functions thus are to be considered as bulky substituents.

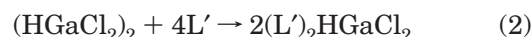
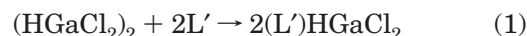
Introduction

Dichlorogallane $(HGaCl_2)_2$ is one of the most readily accessible gallium hydrides: Readily prepared in quantitative yield from anhydrous $(GaCl_3)_2$ and a trialkylsilane R_3SiH , without any solvent, it is stable below 0 °C and soluble in many common solvents, which makes it a convenient starting material for gallium chemistry.^{1,2} Its complexes and its conversion into other molecular gallium halides, chalcogenides, and pnictides have recently been investigated extensively.^{3–6} In this context, *pyridines* were shown to be the most suitable ligands L in the coordination chemistry of dichlorogallane, and a series of complexes of the types $(L)HGaCl_2$ and $(L)_2HGaCl_2$ have been studied.⁴ In the present

account we report two unusual side-reactions that were observed during experiments with the complexes with $L = 3,5$ -dimethylpyridine (L').

Preparative and Structural Results

Dehydrogenative Coupling. The complexes $(L')HGaCl_2$ and $(L')_2HGaCl_2$ are obtained from reactions of the components in the appropriate molar ratio according to eqs 1 and 2. The former has a tetrahedral structure, while the latter is best described as based on a trigonal bipyramid (tbp) with the ligands L' in axial positions.⁴ The 1:1 complex is stable, but solutions of the 2:1 complex have now been found to evolve molecular hydrogen in boiling toluene (ca. 110 °C). The reaction gives a ca. 90% isolated yield of the dinuclear product of dehydrogenative Ga–Ga coupling (eq 3), which can be separated from the excess ligand released in the process by crystallization. It thus appears that the second ligand L' and therefore a tbp structure is responsible for the activation of the Ga–H function for dehydrogenative coupling.



($L' = 3,5$ -dimethylpyridine)

The product $(L')Cl_2Ga-GaCl_2(L')$ is a colorless, crystalline solid of high thermal stability (mp 228 °C), which was readily identified by its analytical and spectroscopic data (Experimental Part). The NMR spectra of solutions in CD_2Cl_2 have shown that the compound is diamagnetic and that the L' ligands are equivalent and have local C_{2v} symmetry. The 1H resonance of the Ga–H function present in the NMR spectrum of $(L')HGaCl_2$ has disappeared, as has the $\nu(Ga-H)$ stretching frequency in the IR spectrum.

Crystals grown from toluene are monoclinic, space group $C2/m$, with $Z = 2$ formula units (of point group symmetry C_{2h}) in the unit cell. The asymmetric unit contains one quarter of the dinuclear molecule, the remainder being generated by symmetry (Figure 1). The carbon and nitrogen atoms of both ligands L' and the two gallium atoms reside in a crystallographic mirror plane. The substituents of the two tetrahedrally coordinated gallium atoms are in a staggered *anti*-conformation. Note also that the orientation of the two pyridine molecules is staggered, i.e., bisecting both Cl–

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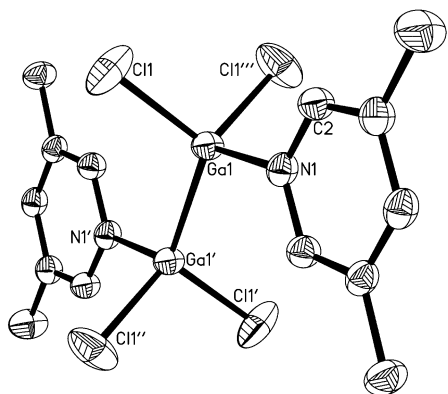
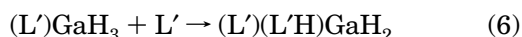
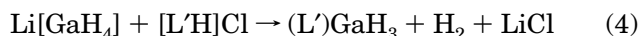


Figure 1. Molecular structure of $(L')Cl_2Ga-GaCl_2(L')$ (ORTEP, 50% probability ellipsoids, H atoms omitted). The molecule has C_{2h} symmetry. Selected bond lengths [Å] and angles [deg] (with standard deviations): Ga1–Ga1' 2.4000(8), Ga1–N1 2.015(4), Ga1–Cl1 2.189(1), N1–C2 1.342(6), C2–C3 1.373(7), C3–C4 1.399(6), C4–C5 1.387(7), C5–C6 1.379(6), C6–N1 1.348(6); Cl1–Ga1–Cl1' 105.71(7), Cl1–Ga1–N1 101.31(7), Cl1–Ga1–Ga1' 117.03(3), N1–Ga1–Ga1' 112.2(1).

Ga–Cl angles. The Ga–Ga' distance of 2.4000(8) Å represents a true single bond and is in good agreement with reference data.⁷ The four equivalent Ga–Cl bond lengths are rather short, at 2.1886(10) Å, and together with the equally short Ga–N distances of 2.015(4) Å also indicate tight bonding of all substituents to the dinuclear Ga–Ga unit.

Hydrogallation. The reaction of lithium gallium hydride $Li[GaH_4]$ with equimolar quantities of 3,5-dimethylpyridinium chloride $[L'H]Cl$ in diethyl ether at -78 °C affords the 1:1 adduct $(L')GaH_3$ in ca. 70% yield (mp 67 °C with decomposition) (eq 4).⁴ It has now been observed that this product undergoes slow decomposition upon storage at room temperature to give gaseous hydrogen H_2 , gray particles of metallic gallium, and orange crystals of a new complex, which was identified as the hydrogallation product $(HL')(L')GaH_2$. The decomposition can thus be formulated as proposed in eq 5. This mass balance suggested that a ligand L' liberated in the decomposition of a complex $(L')GaH_3$ is the substrate for hydrogallation by a second molecule of the complex. Therefore the same product should be accessible by treating $(L')GaH_3$ with excess ligand L' , and solutions of the complex in L' without a solvent were indeed found to give the hydrogallation product after 72 h at 20 °C (eq 6). Separation of the $(L'H)(L')GaH_2$ complex from excess ligand proved to be difficult, and only a few crystals of pure material could be grown for characterization in both cases. The yields are estimated to be ca. 50% for eqs 5 and 6. Elemental analysis of the bulk material was not satisfactory.



The orange crystals are stable at room temperature and can be readily dissolved in benzene. The NMR spectra of the solutions show two sets of 1H and ^{13}C resonances, which can be assigned to one unchanged

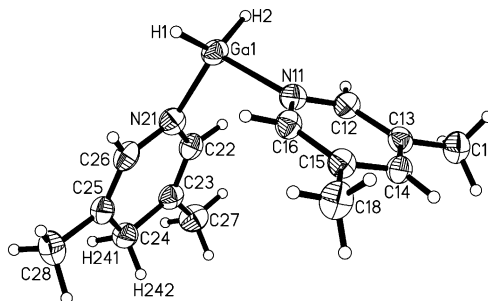


Figure 2. Molecular structure of $(L')(L'H)GaH_2$ (ORTEP, 50% probability ellipsoids for the heavier atoms, arbitrary radii for hydrogen atoms) Selected bond lengths [Å] and angles [deg] (with standard deviations): Ga1–H1 1.40(3), Ga1–H2 1.47(3), Ga1–N11 2.072(2), Ga1–N21 1.898(2), N11–C12 1.341(3), C12–C13 1.385(4), C13–C14 1.388(4), C14–C15 1.387(4), C15–C16 1.385(4), C16–N11 1.342(3); N21–C22 1.392(3), C22–C23 1.344(4), C23–C24 1.497(4), C24–C25 1.501(4), C25–C26 1.337(4), C26–N21 1.390(4); H1–Ga1–H2 127(2), N11–Ga–N21 102.6(1), H1–Ga1–N11 99(2), H1–Ga1–N21 109(1), H2–Ga1–N11 105(1), H2–Ga1–N21 111(1).

ligand L' and to a ligand that is monohydrogenated in the 4-position (Experimental Part). Both ligands appear to have local C_{2v} symmetry, which notably includes the equivalence of the two protons in the 4-position of the hydroppyridyl ligand. The resonances of these protons and of their common carbon atom $C^4(L'H)$ appear in the *aliphatic* region at δ 3.21 and 36.0 ppm, respectively, while those of the HC^4 unit in the pyridine ligand L' remain in the *aromatic* region at δ 6.55 ($^1HC^4$) and 138.8 ppm ($^{13}C^4$).

The hydrogen atoms residing at the gallium atom give rise to a quadrupole-broadened singlet resonance at δ 5.5 ppm with the relative intensity of 2 H. The GaH_2 group can also be traced in the IR spectrum (Nujol on KBr), which shows two bands at 1882 and 1902 cm^{-1} for $\nu(GaH_2)$ vibrations. The absorption bands of the pyridine ligand L' can be identified by comparing the data with those of the $(L')GaH_3$ complex, but these are clearly complemented by a set of new bands to be assigned to the hydroppyridyl group $L'H$.

Crystals of $(L'H)(L')GaH_2$ are monoclinic, space group $P2_1/n$, with $Z = 4$ molecules in the unit cell. The asymmetric unit contains one molecule, the geometry of which approaches mirror symmetry quite closely (Figure 2). All hydrogen atoms, including in particular those of the GaH_2 group, have been located as demonstrated in the electron density map presented in Figure 3. The pyridine ligand L' and the 4-hydroppyridyl group $L'H$ can be easily distinguished by the extra hydrogen atom at C24 in the latter and by the individual bond lengths and angles.

The distance Ga–N11 = 2.072(2) Å (for Ga– L') is significantly longer than the distance Ga–N21 = 1.898(2) Å (for $L'H$). The former thus qualifies as a donor–acceptor bond, while the latter represents a strong gallium–amide linkage, but both heterocycles (of L' and $L'H$) are yet essentially planar. The C–C and C–N ring

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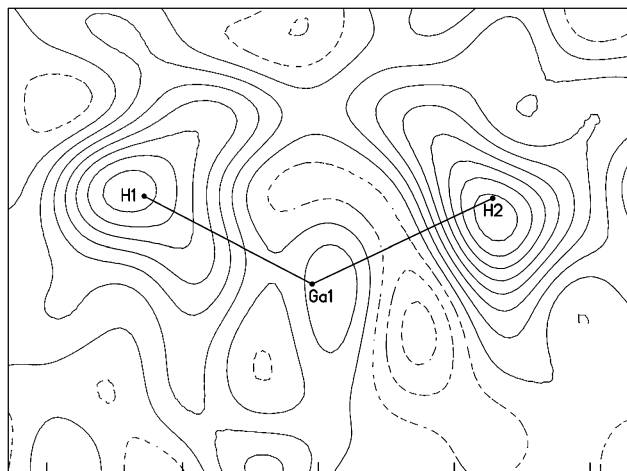


Figure 3. Cross section through the electron density difference map in the H1–Ga1–H2 plane illustrating the hydride locations in $(L')(L'H)GaH_2$. The map was obtained using phases based on all atoms except H1 and H2, and the final refined positions are superimposed. Contours are drawn at an interval of $0.1 \text{ e}/\text{\AA}^{-3}$. Positive and negative contours are shown as solid and dashed lines, respectively.

distances of L' are similar to those found, for example, in $[(L')GaCl_2]_2$ (above), while for the hydroypyridyl group $L'H$ the short C–C distances C22–C23 = 1.344(4) Å and C25–C26 = 1.337(4) Å indicate localized double bonds, as opposed to the distances C23–C24 = 1.497(4) Å and C24–C25 = 1.501(4) Å, which are proof for C–C single bonds at the hydrogenated carbon atom C24.

It is particularly noteworthy that the angle N11–Ga–N21 is exceedingly small, at $101.59(9)^\circ$, although the bulk of the two large substituents would suggest otherwise. This result means that the two *hydride* substituents at the gallium atom, probably intuitively considered as “small”, require a seemingly unproportional share of space, as indicated by the large angle H1–Ga–H2 of $127(2)^\circ$. This structural result nicely reflects the *hydridic* character of Ga-bound hydrogen atoms. The data also corroborate observations⁴ for $(L')GaH_3$, as well as for complexes with tertiary amines and phosphines,^{8a–f} where the GaH_3 pyramid was consistently found to be surprisingly flat. Quantum-chemical calculations on the phenomenon are in progress.^{8g}

Discussion

The work presented in this short account has shown that *dehydrogenative Ga–Ga coupling* appears to be a general reaction for dichlorogallane and its complexes. This type of elimination had previously been observed for the parent compound $(HGaCl_2)_2$, but in the absence of ligands it leads to the mixed-valent product $Ga-[GaCl_4]$, in which no Ga–Ga bonding is established.

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Homovalent dinuclear complexes have been isolated with $L = PR_3$ ² or other ligands,^{7,9} the structures of which are analogous to that now demonstrated for a pyridine complex. The reaction proceeds on heating of the substrates in toluene. Even under the applied forcing conditions (boiling toluene, excess ligand L') the complexes $(L')GaHCl_2$ and $(L')_2GaHCl_2$ show no *hydrogallation* reactions which would afford hydroypyridyls of the type $[(L'H)GaCl_2]_n$ or $(L')(L'H)GaCl_2$.

By contrast, the complex $(L')GaH_3$ undergoes *pyridine-hydrogallation* even under mild conditions (at room temperature), again provided that excess ligand L' is supplied. Note, however, that at room temperature $(L')GaH_3$ does not add a second equivalent of the ligand L' to give a stable 2:1 complex $(L')_2GaH_3$. Yet the excess ligand applied in the reaction is also activating the Ga–H function for hydrogallation by promoting the transfer of a hydride anion to the 4-position of the pyridine ligand.

The product of the formula $(L')(L'H)GaH_2$ has a pyridine and a 4-hydroypyridyl ligand attached to a common gallium atom. Upon hydride transfer, the aromatic system of the pyridine heterocycle L' with its C–C and C–N bonds of about equal lengths is interrupted in the process as shown by the spectroscopic data of the CH_2 group and the structural data of the ligands L' and $L'H$ listed in the caption to Figure 2. In particular, a comparison of the NMR data of the L' and $L'H$ groups in the compound leads to the same conclusion.

Similar hydrometalation reactions have been observed previously for the reactions of $Li[BH_4]$, $Li[AlH_4]$, and $(Me_3N)AlH_3$ with pyridines.^{10–12} In every example all three or four hydride functions are reported to be involved in the hydrometalation. In one of these reports it has been stated that no similar reaction is observed using $(Me_3N)GaH_3$ as hydridic component.¹² No other gallium hydrides, which have the least hydridic character among the three group 13 element hydrides, had been investigated in the context of the hydrogallation of pyridines. Hydrogallation reactions with other unsaturated substrates are well documented.¹³

Experimental Part

All experiments were carried out in an atmosphere of dry nitrogen. Solvents were dried, distilled, and saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. $(HGaCl_2)_2$, $(L')GaHCl_2$, and $(L')GaH_3$ were prepared as described previously.^{1,2,4} NMR chemical shifts are given in δ values [ppm]

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referring to the residual signals of the deuterated solvent (CD₂-Cl₂, C₆D₆) converted to TMS, and coupling constants *J* are in Hz.

sym-Bis(3,5-dimethylpyridine)tetrachlorodigallium-(Ga-Ga'), (L')₂Ga₂Cl₄. (L')GaHCl₂ (0.300 g, 0.843 mmol) was dissolved in toluene (5 mL) and the solution heated to reflux for 5 h. The solution was filtered from small amounts of a precipitate while hot and allowed to cool slowly to room temperature. After 3 days the crop of colorless crystals was separated by filtration, washed with small portions of hexane (2 × 5 mL), and dried in a vacuum: 0.186 g, 89% yield, mp 228 °C. NMR (CD₂Cl₂, 20 °C), ¹H: 2.46 (s, 12H, Me); 7.79 (s, 2H, HC⁴); 8.56 (s, 4H, HC^{2/6}); ¹³C{¹H}: 18.6 (s, Me); 137.1 (s, C^{3/5}); 144.1 (s, C⁴); 144.4 (s, C^{2/6}). Anal. Found: C 34.08, H 3.61, N 5.63, Cl 27.99. Calcd for C₁₄H₁₈Cl₄Ga₂N₂ (495.56): C 33.93, H 3.66, N 5.65, Cl 28.62.

Dihydro(3,5-dimethylpyridine)(3,5-dimethyl-4-hydro-pyridyl)gallium, (L')(L'H)GaH₂. A sample of colorless, crystalline (L')GaH₃ (ca. 150 mg, 0.83 mmol) was kept in a closed flask under nitrogen at room temperature for 2 months. The material slowly deteriorated, developing a gray precipitate of metallic gallium accompanied by crystal growth in parts of the vessel. On reopening, a slight gas pressure was noticed. The orange crystals (ca. 60 mg) were collected and investigated on the diffractometer, by NMR spectroscopy in benzene solution and by IR spectroscopy in a Nujol mull on KBr disks.

Another sample of colorless, crystalline (L')GaH₃ (200 mg, 1.11 mmol) was dissolved in 3 mL (excess) of L' and the mixture stirred magnetically for 3 days. The color of the solution turned via yellow to orange, and small amounts of gray metallic gallium precipitated. The reaction mixture was filtered, and the pyridine L' was removed from the filtrate in a vacuum to leave a resinous residue containing small crystals of the same product as identified in the above experiment. Its NMR spectra indicated the presence of small amounts of a few unidentified byproducts, which were difficult to separate. No sharp melting point was detected because of rapid decomposition on heating, and elemental analysis was not fully satisfactory. The crude yield is estimated to ca. 50%.

NMR (C₆D₆, 20 °C), ¹H: 1.63 [s, 6H, Me(L')]; 1.77 [s, 6H, Me(L'H)]; 3.21 [s, 2H, H₂C⁴(L'H)], 5.50 [br s, 2H, GaH₂]; 6.52 [s, 2H, HC^{2/6}(L'H)]; 6.55 [s, 1H, HC⁴(L')]; 8.13 [s, 2H, HC^{2/6}(L')]; ¹³C{¹H}: 17.7 [s, Me(L')]; 21.6 [s, Me(L'H)]; 36.0 [s, C⁴(L'H)], 130.7 [s, C^{2/6}(L'H)]; 133.7 [s, C^{3/5}(L')]; 138.8 [s, C⁴(L')]; 146.5 [s, C^{2/6}(L')]; C^{2/5}(L') was not detected because of overlap with the solvent signal. IR (Nujol, KBr): 1882 and 1902 cm⁻¹ (s) ν(GaH₂); 1676, 1629, 1601, 1314, 1246, 1174, 1148, 1092, 1045, 986, 963, 942, 862, 802, 722, 703, 680, 600, 538 cm⁻¹ for L' and L'.

Determination of the Crystal Structures. Specimens of suitable quality and size of (L')₂Ga₂Cl₄ and (L')(L'H)GaH₂ were

Table 1. Crystal Data, Data Collection, and Structure Refinement for Compounds (L')₂Ga₂Cl₄ and (L')(L'H)GaH₂

	(L') ₂ Ga ₂ Cl ₄	(L')(L'H)GaH ₂
empirical formula	C ₁₄ H ₁₈ Cl ₄ Ga ₂ N ₂	C ₁₄ H ₂₁ GaN ₂
<i>M</i>	495.56	287.05
cryst syst	monoclinic	monoclinic
space group	<i>C</i> 2/ <i>m</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	17.1994(3)	8.0226(3)
<i>b</i> /Å	7.3604(2)	10.9023(4)
<i>c</i> /Å	8.6468(2)	16.8366(7)
<i>b</i> /deg	117.0185(10)	100.895(2)
<i>V</i> /Å ³	975.17(4)	1446.07(10)
ρ _{calc} /g cm ⁻³	1.688	1.318
<i>Z</i>	4	4
<i>F</i> (000)	492	600
<i>T</i> /K	143	143
no. of refls measd	10 964	43 260
no. of refls unique	974	2615
no. of params/restraints	87/0	238/0
R1 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0351	0.0334
wR2 ^a	0.0937	0.0749
weighting scheme	<i>a</i> = 0.0541 <i>b</i> = 3.5706	<i>a</i> = 0.0254 <i>b</i> = 0.8985
σ _{fin} (max/min)/e Å ⁻³	3.046/−0.452	0.240/−0.248

$$^a \text{wR2} = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3.$$

mounted on the ends of quartz fibers in inert perfluoropoly-alkyl ether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on *F*² (SHELXL-97).¹⁴ The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located and refined with isotropic displacement parameters. Absorption corrections for both structures were carried out using DELABS, as part of the PLATON suite of programs.¹⁵ Further information on crystal data, data collection, and structure refinement is summarized in Table 1.

Acknowledgment. This work was generously supported by Fonds der Chemischen Industrie.

Supporting Information Available: Details about the X-ray crystal structures in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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