Syntheses and structures of quinuclidine-stabilized four- and five-coordinate mono- and di-chlorogallane

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Hydride/chloride redistribution reactions provided high yields of GaCl$_2$H(quin) I, GaCl$_2$H(quin)$_2$ II, GaClH$_2$(quin) III and GaClH$_2$(quin)$_2$ IV(quin = quinuclidine) and structural characterization of compounds II and IV authenticate the unusual five-coordinate geometry for gallium hydride complexes.

Organogallium compounds are used extensively to prepare solid state materials such as GaN.[1] In metal organic chemical vapor deposition (MOCVD) processes, for instance, the high volatility, long shelf-life and chemical reactivity of compounds such as GaMe$_3$ have made them especially attractive molecular precursors. One of the drawbacks of organogallium compounds is the presence of direct Ga–C bonds that can lead to unwanted incorporation of carbon into the solid state product. In sensitive opto-electronic devices such as lasers, even trace quantities of carbon can seriously degrade performance.[2] Replacement of the carbon-based ligands with hydrides appears as an attractive alternative but suffers from the lower stability and more difficult syntheses of the compounds. We report in this paper the preparation and structure of mono- and di-chlorogallanes stabilized by quinuclidine. Strong donors, including trimethylamine,[3,4] quinuclidine[5] and tricyclohexylphosphine,[6] stabilize GaH$_3$, which in the absence of the donor exists as Ga$_2$H$_6$ and decomposes above −30 °C.[7] The presence of chloro ligands offers attractive synthetic routes to molecules that can be used as single source precursors in CVD processes.

Unstabilized mono- and di-chlorogallane have been synthesized by the reaction of GaCl$_3$ with trimethylsilane[8,9] and have been stabilized by direct reaction with donors. Chloride/hydride exchange has proven to be successful for the syntheses of other substituted gallanes,[10,11] and the following alternative routes bypass the need to prepare and purify [GaClH$_2$]$_2$ and [GaCl$_2$H]$_2$. All reactions were conducted under an atmosphere of prepurified nitrogen. A diethyl ether (20 mL) solution of GaCl$_3$ (0.957 g, 5.44 mmol) was added to a stirred, 30 mL ether solution of GaH$_3$(quin) (quin = quinuclidine) (0.500 g, 2.72 mmol) at room temperature over a period of 1 h. The resulting mixture was stirred at room temperature for an additional 6 h, at which point an additional equivalent of quinuclidine (5.44 mmol) dissolved in ether was added. This delayed addition of quinuclidine facilitated the ligand redistribution reaction [eqn. (1)], which presumably required an available coordination site

$$2\ GaCl_3 + GaH_3(quin) + 2\ quin \rightarrow 3\ GaCl_2H(quin) \quad (1)$$
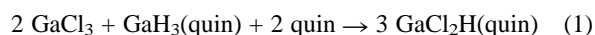
on the gallium. The reaction mixture was stirred for another 14 h, then filtered. Upon concentration and storage at −15 °C, the colorless filtrate yielded 1.65 g (80% yield) of crystalline GaCl$_2$H(quin) I.[12] Compound I decomposed without melting at 92 °C. Chemical ionization mass spectrometry revealed the presence of an intense parent ion (plus one) at *m/z* 252. A strong v_{GaH} (KBr pellet) was observed in I at 1946 cm^{-1}; however, no hydride resonance was observed in ^{1}H NMR spectrum. Compound I was also prepared in 25% yield by addition of quinuclidine to an ether suspension comprised of 4 equiv. of LiH and 1 equiv. of [NH$_4$][GaCl$_4$].

Reaction of I with one equivalent of quinuclidine at room temperature in ether produced the bis(quinuclidine) adduct in high yield. Needle-like crystals of GaCl$_2$H(quin)$_2$ II,[13] were

stable up to 174 °C and appeared to decompose gradually above this temperature. Coordination of the second ligand shifted the v_{GaH} to 1882 cm^{-1}. While AlH$_3$ and related aluminium hydrides form many five-coordinate structures, this is uncommon in gallium hydride chemistry where the only reported examples of five-coordinate hydrido complexes of gallium contain chelating ligands.[14–17]

Crystalline monochlorogallane derivative, GaClH$_2$(quin) III, was synthesized in 81% yield by the related ligand redistribution reaction shown in eqn. (2).

$$GaCl_2H(quin) + GaH_3(quin) \rightarrow 2\ GaClH_2(quin) \quad (2)$$
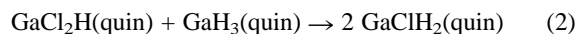
Following addition of an ether solution of GaH$_3$(quin) to an ether solution of I, the reaction mixture was refluxed for 40 h. After filtration and concentration, crystals of III[18] were isolated upon cooling the solution to −15 °C. The v_{GaH} (KBr) was lowered to 1892 cm^{-1}, characteristic of replacing one of the electronegative chloro ligands in I with a hydride. In addition to resonances from the quinuclidine ligand, the ^{1}H NMR spectrum (in C$_6$D$_6$) displayed a broad resonance at δ 5.14 assignable to the GaH$_2$ unit.

Reaction of III with excess quinuclidine in refluxing ether followed by crystallization at −15 °C formed the five-coordinate complex, GaH$_2$Cl(quin)$_2$ IV.[19] Batches of crystalline IV typically exhibited three absorptions (1891s, 1852m and 1817w cm^{-1}) in the Ga–H stretching region of the IR spectrum (KBr). Given the symmetry of the compound (*vide infra*), we expect only two absorptions and suggest that the crystals were mixtures of III and IV. Thus, only the peaks at 1852 and 1817 cm^{-1} are assigned to IV. These are similar to the values of 1854 and 1837 cm^{-1} reported for GaH$_2$[2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$].[16] This interpretation was consistent with the elemental analytical data that were always closer to the values calculated for III.

Compounds I, II and IV were characterized using single crystal X-ray crystallography. Each molecule of I sits on a crystallographic mirror plane that passes through Ga(1), N(1) and H(1) in addition to three of the quinuclidine carbons (Fig. 1).[20] The hydride ligand was located, and its position and isotropic thermal parameters were refined. The basic arrangement of the four ligands is that of a slightly distorted tetrahedron where the angles listed in the figure caption show that the larger, heavy atom ligands are splayed back away from the hydride.

Despite the observation that bulk samples of IV were contaminated with III, a suitable single crystal was selected for study. The five-coordinate complex IV, sits on a crystallographic twofold axis collinear with the Ga(1)–Cl(1) bond (Fig. 2).[20] The structure is close to a perfect trigonal bipyramid bearing the quinuclidine ligands in the axial positions. The only significant deviation is an enlarged H(1)–Ga(1)–H(1C) angle of 127(2)°. The corresponding Cl(1) Ga(1)–H(1) angles are diminished to 116.9(9)°; a pattern consistent with Bent's rule.[21] Comparing the bond distances of I and IV, we find an increase for all of the heavy atoms for IV appropriate for the increase in coordination number. The Ga–H distances, however, decrease from 1.66(5) Å in I to 1.51(2) Å in IV.

The structure of the five-coordinate dichlorogallane II, was also trigonal bipyramidal; however, the hydride was not located (Fig. 3).[20] As in the structure of IV, small angular deviations from the ideal geometry were observed and were consistent
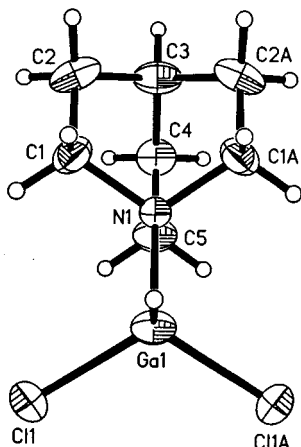
Fig. 1 Structure of **I** showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.017(3), Ga(1)–H(1) 1.66(5), Ga(1)–Cl(1) 2.185(1); N(1)–Ga(1)–Cl(1) 103.40(6), Cl(1)–Ca(1)–Cl(1A) 108.24(6), N(1)–Ga(1)–H(1) 110(2), Cl(1)–Ga(1)–H(1), 115.2(8).
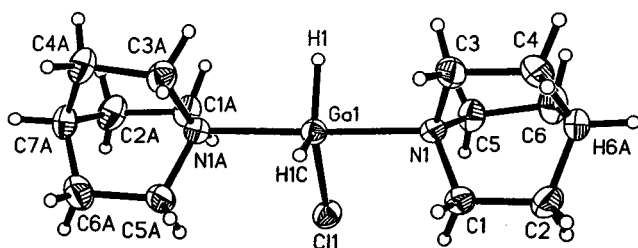
Fig. 2 Structure of **IV** showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.259(2), Ga(1)–H(1) 1.51(2), Ga(1)–Cl(1) 2.2653(8); N(1)–Ga(1)–N(1A) 178.25(9), N(1)–Ga(1)–Cl(1) 90.88(4), N(1A)–Ga(1)–H(1), 89.1(9), N(1)–Ga(1)–H(1) 90.1(9), Cl(1)–Ga(1)–H(1) 116.6(9), H(1)–Ga(1)–H(1C) 127(2).
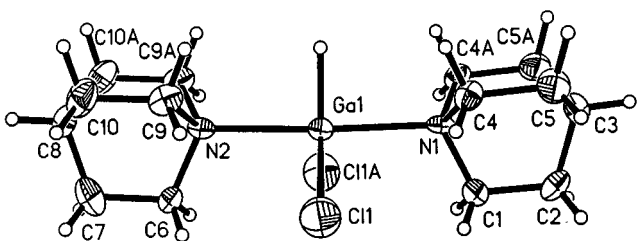
Fig. 3 Structure of **II** showing 50% thermal ellipsoids and the idealized position of the hydride ligand. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.254(8), Ga(1)–N(2) 2.232(8), Ga(1)–Cl(1) 2.246(2); N(1)–Ga(1)–N(2) 177.2(3), Cl(1)–Ga(1)–Cl(1A) 113.0(2), Cl(1)–Ga(1)–N(1) 91.0(1), Cl(1)–Ga(1)–N(2) 90.5(1).

with Bent's rule. The crystallographically independent Ga–N distances [2.254(8) and 2.232(8) Å] were similar the value found in **IV** [2.259(2) Å].

All attempts to prepare the five-coordinate trichlorogallium complex, GaCl$_3$(quin)$_2$, were unsuccessful and always resulted in nearly quantitative isolation of GaCl$_3$(quin) **V**.[22] It is intriguing that the five-coordinate geometry is only stable enough relative to the four-coordinate structure to allow isolation with the mixed H/Cl ligand complexes. While replacing hydrides with chlorides will increase the Lewis acidity, it will also increase the steric repulsion. Our results suggest that the maximum stability is achieved in **IV** where two chlorides and one hydride are present. Quinuclidine does not differ qualitatively from other donors, rather the combination of improved donor strength and smaller cone angle causes a quantitative shift in the appropriate equilibria that stabilize the five-coordinate products.

Notes and references

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12 Compound **I**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C); δ 0.76 (6H, m, CH$_2$), 0.95 (1H, m, CH), 2.53 (6H, t, NCH$_2$). Anal. Calc. for C$_7$H$_{14}$Cl$_2$GaN: C, 33.26; H, 5.58; N, 5.54. Found: C, 32.28; H, 5.98; N, 5.45%.
13 Compound **II**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C); δ 0.99 (6H, m, CH$_2$), 1.22 (1H, m, CH), 2.64 (6H, t, NCH$_2$). Anal. Calc. for C$_{14}$H$_{27}$Cl$_2$GaN$_2$: C, 46.19; H, 7.48; N, 7.70. Found: C, 45.80; H, 7.72; N, 7.62%.
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18 Compound **III**: mp: 89 °C, (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 0.82 (6H, m, CH$_2$), 1.04 (1H, m, CH), 2.49 (6H, t, NCH$_2$), 5.14 (2H, br s, GaH$_2$). Anal. Calc. for C$_7$H$_{15}$ClGaN: C, 38.50; H, 6.92; N, 6.41. Found: C, 38.27; H, 7.11; N, 6.30%.
19 Compound **IV**: MS (CI): 329.1 (11.8%, [(C$_7$H$_{13}$N)$_2$GaClH$_3$]$^+$), 293.2 (15.7%, [(C$_7$H$_{13}$N)$_2$GaH$_2$]$^+$), 216.0 (16.0%, [C$_7$H$_{13}$NGaClH$_2$]$^+$), 182.0 (19.9%, C$_7$H$_{13}$NGaH$_2$]$^+$), 112.1 (100%, [C$_7$H$_{13}$NH]$^+$).
20 *Crystal data*: **I**: C$_7$H$_{14}$Cl$_2$GaN, M = 252.81, orthorhombic, space group *Pbcm*, a = 6.0102(2), b = 15.8808(3), c = 10.7925 (3) Å, V = 1030.11(5) Å^3, T = 173(2) K, Z = 4, μ = 3.132 mm^{-1}, 6030 reflections collected, 962 independent reflections, 853 with $I > 2\sigma(I)$, R_1 = 0.0338, wR_2 = 0.0802.

  IV: C$_{14}$H$_{28}$ClGaN$_2$, M = 329.56, orthorhombic, space group *Pbcn*, a = 10.9098(2), b = 12.0848(2), c = 12.3099(3) Å, V = 1622.97(6) Å^3, T = 173(2) K, Z = 4, μ = 1.847 mm^{-1}, 8527 reflections collected, 1433 independent reflections, 1202 with $I > 2\sigma(I)$, R_1 = 0.0296, wR_2 = 0.0606.

  II: C$_{14}$H$_{23}$Cl$_2$GaN$_2$, M = 359.96, orthorhombic, space group *Pmn2$_1$*, a = 10.2217(6), b = 12.2916(7), c = 6.4620(4) Å, V = 811.89(8) Å^3, T = 173(2) K, Z = 2, μ = 2.013 mm^{-1}, 4661 reflections collected, 1458 independent reflections, 1321 with $I > 2\sigma(I)$, R_1 = 0.0529, wR_2 = 0.1365. CCDC 182/1093. See http://www.rsc.org/suppdata/cc/1999/123/ for crystallographic files in .cif format.
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22 Compound **V**: mp 239–245 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 0.66 (m, 6H, CH$_2$), 0.89 (m, 1H, CH), 2.62 (t, 6H, NCH$_2$). Anal. Calc. for C$_7$H$_{13}$NGaCl$_3$: C, 29.27; H, 4.56; N, 4.88. Found: C, 29.48; H, 4.98; N, 4.81%.

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