# A $Ga_4N_8$ cage structure formed by reaction of trimethylgallium with phenylhydrazine

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# Methane elimination during thermolysis of GaMe<sub>3</sub> with PhHNNH<sub>2</sub> yields sequentially dimeric [Me<sub>2</sub>Ga{ $\mu$ -N(H)N(H)Ph}]<sub>2</sub>, tetrameric [MeGa{ $\mu$ -N(H)NPh}]<sub>4</sub> and, ultimately, GaN; the X-ray structure of the tetramer shows a novel Ga<sub>4</sub>N<sub>8</sub> cage.

A number of research groups have investigated the chemistry of molecules containing Ga–N bonds,<sup>1–5</sup> with most of the recent emphasis directed at using these compounds as single-source precursors to the wide bandgap semiconductor GaN.<sup>6–13</sup> Here we describe some new results on the use of hydrazines as a source of nitrogen including the formation of two intermediates formed on elimination of 1, then 2 equiv. of methane during the thermolysis reaction between GaMe<sub>3</sub> and PhHNNH<sub>2</sub>. Both complexes have been isolated and fully characterized and the latter is shown to have an unusual structure featuring a cage with a Ga<sub>4</sub>N<sub>8</sub> core;<sup>14</sup> this species eliminates a final equivalent of methane to form GaN at higher temperatures.

As shown in Scheme 1, I equiv. of methane is eliminated in the reaction of GaMe<sub>3</sub> and PhHNNH<sub>2</sub> at room temperature in toluene. We saw no evidence for the presumed monomeric intermediate 'Me<sub>2</sub>Ga–N(H)N(H)Ph', instead the colorless dimeric product was isolated in 88% yield.<sup>15</sup>

2GaMe<sub>3</sub> + 2H<sub>2</sub>N-NHPh 
$$\xrightarrow{\text{toluene, 20 °C}}_{-2MeH} \xrightarrow{\text{PhHN}} N \xrightarrow{\text{Me}}_{Ga} \xrightarrow{Me}_{N+Ph} N$$

### Scheme 1

The solid-state structure of the dimer is very similar to that of the closely related species  $[Et_2Ga\{\mu-N(H)NPh_2\}]_2$ , prepared by the metathesis reaction between  $Et_2GaCl$  and  $LiN(H)NPh_2$ ,<sup>11</sup> with both compounds crystallizing as *anti* conformers.<sup>16</sup>

Upon further heating, the dimer undergoes a second methane elimination reaction as shown in Scheme 2.



### Scheme 2

As monitored by <sup>1</sup>H NMR spectroscopy, the reaction proceeds in a quantitative fashion and microcrystalline product, which is much less soluble than the starting material, precipitates from the reaction solvent in 84% yield.<sup>15</sup> The <sup>1</sup>H NMR spectrum shows a simple pattern consistent with only single methyl, N–H and phenyl environments<sup>15</sup> and we saw no evidence of fluxional behavior between -80 and 110 °C. Since these data were insufficient to unambiguously determine the structure of the molecule, an X-ray study was carried out.

Crystals of  $[MeGaN(H)NPh]_4$  were grown by thermolysis of  $[Me_2GaN(H)N(H)Ph]_2$  in toluene at 105 °C.<sup>17</sup> The solid state

structure, shown in Fig.1, consists of a tetrameric unit that resides on the intersection of three mutually perpendicular mirror planes. The geometry about gallium is distorted tetrahedral, with angles ranging from 121.3(1) [N(1)–Ga(1)– C(1)] to 94.4(1) [N(2\*)-Ga(1)-N(2\*)]. The bond length of Ga to the four-coordinate  $N(2^*)$  [1.993 (3) Å] is longer than that to the three-coordinate N(1) [1.914(2) Å], although the mean Ga-N distance of 1.966(3) Å falls within the reported range for gallium amido complexes.<sup>1-5</sup> The N-N bond length of 1.489(3) Å is longer than in the only other crystallographically characterized Ga hydrazide complex  $[Et_2Ga{\mu-N(H)NPh_2}]_2$ , [1.457(8) and 1.446(8) Å $]^{11}$  and is somewhat longer than predicted for a N–N single bond (1.454 Å), a result that may be attributed to the bridging nature of the hydrazine ligand<sup>18</sup> in the cage species. Owing to the high quality of the data obtained, the hydrazine hydrogen was located in the Fourier difference map and refined isotropically. Fig. 2 shows a view of the unit cell which highlights the rather large open core of the structure (ca. 4.5 Å) and the fact that there are no unusually short intermolecular contacts. We are unaware of previous reports of such a cage structure for Ga, although we note that a related boron compound [ButBN(H)N(H)]<sub>4</sub> was characterized some time ago.19

Thermolysis of the cage complex at 700 °C under a hydrogen atmosphere leads to the formation of hexagonal GaN (identified



Fig. 1 X-Ray crystal structure of [MeGaN(H)NPh]<sub>4</sub>





Fig. 2 Unit cell of [MeGaN(H)NPh]<sub>4</sub>

by powder X-ray diffraction by comparison to a standard sample in the JCPDS database) along with a mixture of unidentified volatile organic fragments. Further studies are in progress and will be described in a more detailed account.

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# **Notes and References**

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- 15 Satisfactory elemental analyses (C, H, N) were obtained for all compounds. Experimental details and spectroscopic data are provided as supplementary information.
- 16 Details will be given in a full paper.
- 17 *Crystallographic* data [MeGaÑ(Ĥ)NP]<sub>4</sub>,  $C_{28}H_{36}Ga_4N_8$ ,  $M_w = 763.53$ , tetragonal, space group  $I4_1/a$  (no. 88), a = 14.0460(2), c = 15.581(2) Å, U = 2970.81(6) Å<sup>3</sup>, Z = 4,  $D_c = 1.71$  g cm<sup>-3</sup>, graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.710$  69 Å),  $\mu$ (Mo-K $\alpha$ ) = 36.3 cm<sup>-1</sup>. A total of 6973 reflections (1433 unique,  $R_{int} = 2.73\%$ ) were collected on a colourless crystal of dimensions  $0.24 \times 0.29 \times 0.31$  mm at -111 °C on a Siemens SMART diffractometer/CCD area detector; an empirical absorption correction was applied. The structure was solved by direct methods and refined by full matrix least squares procedures. All non-hydrogen atoms were refined isotropically. The hydrogen atom on N(1) was located from the Fourier difference map and refined isotropically. Final residuals at convergence were R = 0.0227 and  $R_w = 0.0221$  for 1046 data with  $F^2 > 3\sigma(F^2)$  and GOF = 1.23. CCDC 182/782.
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