A Ga_4N_8 cage structure formed by reaction of trimethylgallium with phenylhydrazine

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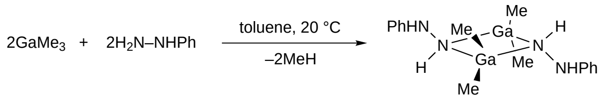
Methane elimination during thermolysis of $GaMe_3$ with $PhHNNH_2$ yields sequentially dimeric $[Me_2Ga\{\mu\text{-}N(H)N(H)Ph\}]_2$, tetrameric $[MeGa\{\mu\text{-}N(H)NPh\}]_4$ and, ultimately, GaN; the X-ray structure of the tetramer shows a novel Ga_4N_8 cage.

A number of research groups have investigated the chemistry of molecules containing Ga–N bonds,[1–5] with most of the recent emphasis directed at using these compounds as single-source precursors to the wide bandgap semiconductor GaN.[6–13] 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 $GaMe_3$ and $PhHNNH_2$. Both complexes have been isolated and fully characterized and the latter is shown to have an unusual structure featuring a cage with a Ga_4N_8 core;[14] this species eliminates a final equivalent of methane to form GaN at higher temperatures.

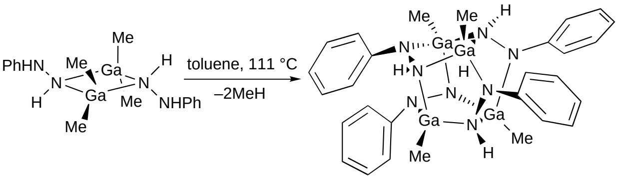
As shown in Scheme 1, 1 equiv. of methane is eliminated in the reaction of $GaMe_3$ and $PhHNNH_2$ at room temperature in toluene. We saw no evidence for the presumed monomeric intermediate '$Me_2Ga–N(H)N(H)Ph$', instead the colorless dimeric product was isolated in 88% yield.[15]



Scheme 1

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

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



Scheme 2

As monitored by ^1H 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.[15] The ^1H NMR spectrum shows a simple pattern consistent with only single methyl, N–H and phenyl environments[15] 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.[17] 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.[1–5] The N–N bond length of 1.489(3) Å is longer than in the only other crystallographically characterized Ga hydrazide complex $[Et_2Ga\{\mu\text{-}N(H)NPh_2\}]_2$, [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[18] 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 $[Bu^tBN(H)N(H)]_4$ 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

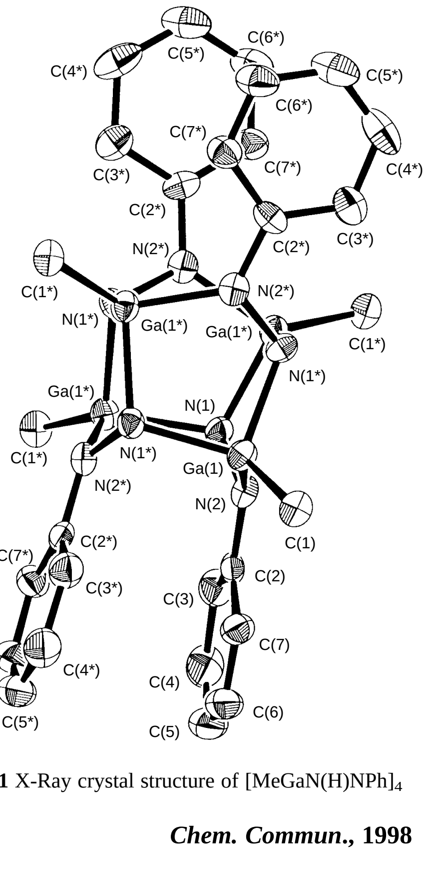


Fig. 1 X-Ray crystal structure of $[MeGaN(H)NPh]_4$

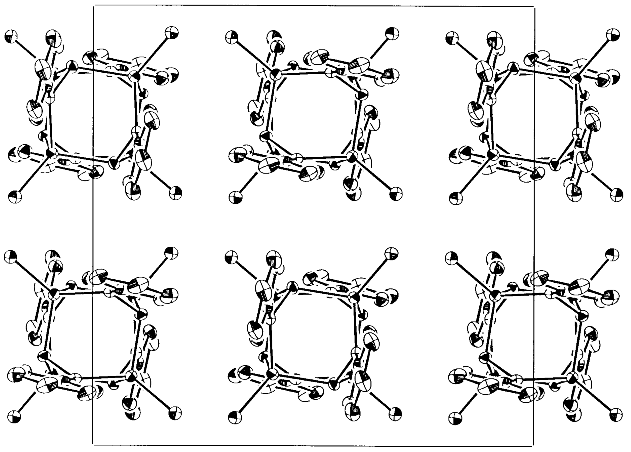


Fig. 2 Unit cell of $[MeGaN(H)NPh]_4$

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* $[MeGaN(H)NP]_4$, $C_{28}H_{36}Ga_4N_8$, $M_w = 763.53$, tetragonal, space group $I4_1/a$ (no. 88), $a = 14.0460(2)$, $c = 15.581(2)$ Å, $U = 2970.81(6)$ Å^3, $Z = 4$, $D_c = 1.71$ g cm^{-3}, graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 36.3 cm^{-1}. 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 $R_w = 0.0281$ for 1046 data with $F^2 > 3\sigma(F^2)$ and GOF = 1.23. CCDC 182/782.

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