

### **Analysis of the GED pattern on the assumption that the vapour species is $\text{Me}_2(\text{H})\text{N}\cdot\text{GaH}_3$**

The MP2/6-311++G(df,p) calculations justify the assumption of local  $C_{3v}$  symmetry for the  $\text{GaH}_3$  and each of the dimensionally equivalent  $\text{CH}_3$  groups, the  $C_3$  axis of which is taken to coincide with the C–N bond. In addition to the five bond distances Ga–N, Ga–H, N–C, N–H and C–H, seven angles (as specified in Table S2 of the supplementary information) have then been used to define the structure. The results of the MP2/6-311++G(df,p) calculations were brought into play as restraints on the parameters that alone did not yield to satisfactory refinement (Table S3), and the SARACEN method,<sup>11</sup> as incorporated in the ed@ed program,<sup>19</sup> was employed to enable free refinement of as many geometric and vibrational parameters as possible. Angles defining twisting of  $\text{GaH}_3$  about the Ga–N bond and of  $\text{CH}_3$  about each of the C–N bonds, as well as rocking of the  $\text{GaH}_3$  group returned values and estimated standard deviations (e.s.ds) effectively set by the restraints, indicating that the experimental data provided no additional information about these parameters. Accordingly, the relevant angles were simply fixed at the calculated values. With appropriate restraints in place, most of the significant amplitudes yielded to refinement; those determined only by the restraints were subsequently assigned values tied to the refined amplitudes of related vectors.

**Table S1(a).** Calculated Optimised Molecular Geometry for  $\text{Me}_2(\text{H})\text{N}\cdot\text{GaH}_3$  Using *Ab Initio* Methods and Various Basis Sets (Distances in pm, Angles in deg).

parameter	basis set/method					
	6-31G*/HF	6-31G*/MP2	6-311G(d,p)/ MP2	6-311+G(d,p)/ MP2	6-311G(df,p)/ MP2	6-311+G(df,p)/ MP2
$r(\text{Ga-N})$	213.4	211.9	214.9	215.2	213.7	213.9
$r(\text{Ga-H4})$	158.8	159.8	158.8	158.8	159.2	159.2
$r(\text{Ga-H5})$	158.9	159.8	158.7	158.7	159.1	159.1
$r(\text{N-H})$	100.4	101.6	101.1	101.4	101.3	101.3
$r(\text{N-C})$	146.8	147.5	147.3	147.3	147.0	147.0
$\angle\text{H4-Ga-N}$	99.1	97.9	97.6	97.5	97.8	97.6
$\angle\text{H5-Ga-N}$	99.8	100.0	99.1	98.9	99.0	97.6
$\angle\text{Ga-N-C}$	111.5	110.9	111.4	111.5	111.4	111.4
$\angle\text{C-N-C}$	112.2	111.2	111.6	111.6	111.6	111.6
$\angle\text{H-N-C}$	108.3	108.3	108.3	108.2	108.5	108.5

**Table S1(b).** Calculated Optimised Molecular Geometry for Me<sub>2</sub>(H)N·GaH<sub>3</sub> Using a DFT (B3PW91) Model and Various Basis Sets (Distances in pm, Angles in deg).

parameter	basis set		
	6-31G*	6-31G(d,p)	6-311G(d,p)
<i>r</i> (Ga–N)	211.3	210.8	215.5
<i>r</i> (Ga–H4)	157.7	158.3	157.9
<i>r</i> (Ga–H5)	157.8	158.3	157.9
<i>r</i> (N–H)	102.0	101.8	101.7
<i>r</i> (N–C)	147.2	147.1	147.1
<H(4)–Ga–N	98.3	98.4	98.4
<H(5)–Ga–N	99.6	99.1	98.7
<Ga–N–C	110.9	111.1	111.6
<C–N–C	112.4	112.5	112.4
<H–N–C	108.6	108.7	108.5

**Table S2.** Least-squares correlation matrix ( $\times 100$ ) for GED structure refinement of  $[\text{Me}_2\text{NGaH}_2]_2$ .<sup>a</sup>

	$p_5$	$p_6$	$k_1^b$	$k_2^b$
$p_1$	-59	53		
$u_2$			69	72
$k_1^b$				62

<sup>a</sup> Only elements with absolute values  $>50\%$  are listed.

<sup>b</sup> Scale factor.