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# Isomerism of dimeric *cis*-ethene-1,2-di(alkylamido)gallium hydrides and chlorides

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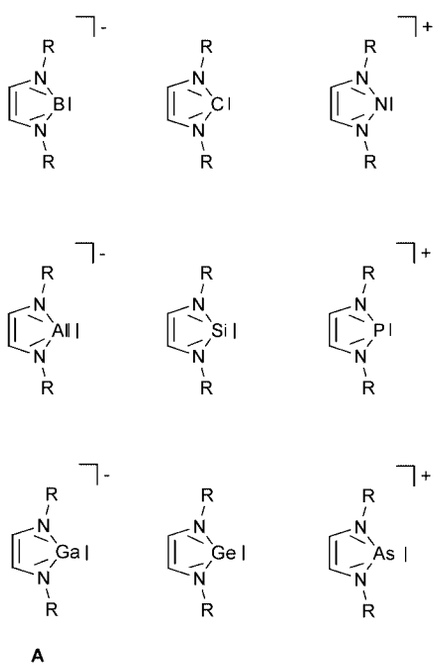
Dichlorogallane $[HGaCl_2]_2$ **1** can be prepared in quantitative yield from equimolar quantities of $GaCl_3$ and $Et_3SiH$ at −13 °C in the absence of a solvent. Treatment of **1** with dilithium *N*,*N*′-di-*tert*-butyl-*cis*-ethenediamide at −78 °C leads to high yields of $[(^tBu_2N_2(CH)_2)GaH]_2$ **2**. According to IR and NMR observations, compound **2** exists in the form of two isomers in benzene solution. Crystallization from pentane affords only one isomer which was identified as a centrosymmetrical dimer with a four-membered ring $(Ga–N)_2$ as the core unit, two hydrogen atoms in *trans* position and two five-membered rings fused to opposite edges also in *trans* position (type **B**). The analogous reaction of $[^tBu_2N_2(CH)_2]Li_2$ with anhydrous $[GaCl_3]_2$ gives the corresponding chloride **3** which exists as only one isomer in solution. Crystals obtained from hexane contain four independent dimeric molecules, all of which have the same structure with inequivalent gallium atoms owing to a redistribution of the chloride ligands. The central four-membered ring $(Ga–N)_2$ has the two five-membered rings fused to neighbouring edges in *trans* position, and the two chlorine atoms are associated with the same gallium atom. This isomer $[^tBu_2N_2(CH)_2]Ga(GaCl_2)$ **3** (type **D**) is unprecedented in the structural chemistry of the "diazabutadiene" complexes of Group 13 elements. The analogous cyclohexyl compound was prepared in high yield following the same route. It is formed as only one isomer which has the centrosymmetrical structure of type **B**, $[(^cHex_2N_2(CH)_2)_2GaCl]_2$ ($^c$Hex = cyclohexyl). The isomerism is probably governed by steric effects.

## Introduction

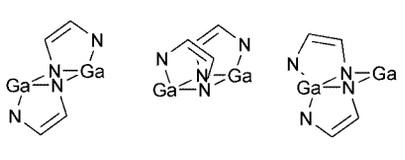
The discovery of stable carbene-type molecules containing low-valent carbon atoms chelated by diazabutadiene ligands ("Arduengo carbenes")[1–3] has stimulated considerable interest in related neutral compounds of the congener elements in the Periodic Table, mainly silicon[4] and germanium.[5] While this work was equally successful, the investigations of the corresponding ionic species have led to only very few examples, mainly with cationic centres at low-valent phosphorus[6] and anionic centres at low-valent gallium[7] (**A** in Scheme 1).

In an effort to improve the pathways to the novel pseudo-aromatic gallium compounds of type **A** we continued our studies of "diazabutadiene (DAB)"† complexes of gallium halides, which are the substrates for the final reduction leading to anionic heterocycles with two-coordinate, low-valent gallium.[7] In the course of this work we decided to include the corresponding hydride molecules, which might open up a cleaner route to anions of type **A**. For this purpose the preparation[8,9] of dichlorogallane $HGaCl_2$ has been revisited and improved.

The literature contains only half a dozen reports on DAB complexes of aluminium[10,11] and gallium,[12–15] but these have already shown some of the important preparative pathways and fundamental structural features of this intriguing class of compounds. We now observed an unprecedented and unexpected isomerism (**B**, **C**, **D**) of the prototype dimers which previously had been encountered in only one configuration (with a centre of inversion: **B** in Scheme 2). Preliminary information on compound **3** was included in a communication.[7]




**Scheme 1** Arduengo carbene type molecules, cations and anions with Group 13, 14 and 15 elements.




**Scheme 2** Isomeric dimers of [(DAB)MX] molecules (M = Al, Ga; X = H, Cl, Br).

† In the previous literature, for ethene-*cis*-1,2-dialkyldiamide ligands of the type $[RNCH{=}CHNR]^{2-}$ the nomenclature "DiAzaButadiene" or "DiAzaButadienide" (DAB) has been used. This terminology is not entirely correct, since diazabutadiene is reduced to the diamide upon reaction with lithium metal. Therefore in this paper the term DAB has been placed in quotation marks for the dianion.

## Results and discussion

### Dichlorogallane 1

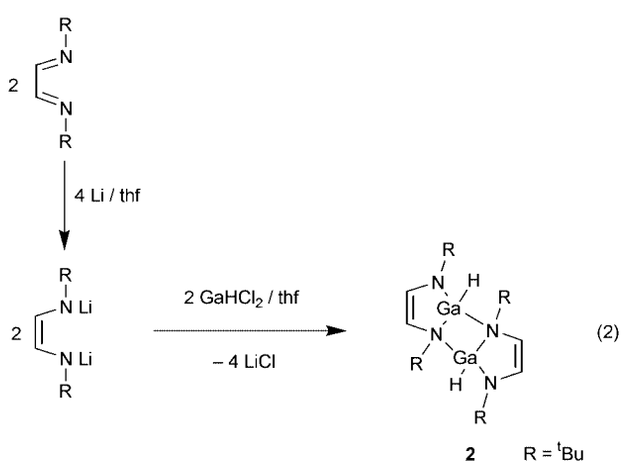
Pure, solvent-free dichlorogallane **1** was first prepared by the reaction of anhydrous gallium trichloride with tri*methyl*silane.[8] This synthesis is somewhat inconvenient since $Me_3SiH$ has a low boiling point (10 °C) and is not commercially available. We have now shown that the preparation is much easier, and equally quantitative, with stoichiometric quantities of tri*ethyl*-silane, which has a more suitable boiling point (107 °C) and is a commercial product [eqn. (1)].

$$(GaCl_3)_2 + 2\ Et_3SiH \longrightarrow 2\ Et_3SiCl + \underset{\mathbf{1}}{(GaHCl_2)_2} \quad (1)$$

The reaction proceeds smoothly at −13 °C without any solvent, and the only by-product, $Et_3SiCl$, is readily removed *in vacuo* at 0 °C, in which $(HGaCl_2)_2$ is perfectly stable.

### *cis*-Ethene-1,2-di(*tert*-butylamido)gallium hydride 2

Dichlorogallane reacts with 1,4-dilithio-1,4-di-*tert*-butyl-1,4-diazabutadiene ($Li_2{}^tBu_2DAB$) in tetrahydrofuran at −78 °C without any obvious decomposition of the labile $[HGaCl_2]_2$ precursor. After warming the reaction mixture to room temperature, evaporation of the solvent, and extraction of the product from the residue with pentane, the expected ($^tBu_2$-DAB)GaH **2** is obtained in 78% yield as a light-yellow solid [eqn. (2)].




Single crystals can be grown from pentane at room temperature, the composition of which has been confirmed by elemental analysis. The mass spectrum (CI) shows the molecular cation of the *dimer* at *m*/*z* 476.

In the IR spectrum of compound **2** two intense absorptions are detected at 1917.7 and 1927.1 $cm^{-1}$ which can be assigned to Ga–H stretching vibrations.[8,9] Surprisingly, the $^1H$ and $\{^1H\}^{13}C$ NMR spectra show *four* sets of signals each for the *tert*-butyl groups and for the CH units in roughly equal intensity. Two broad signals at $\delta$ 5.67 and 6.19 can be assigned to gallium-bound protons. These results may indicate the presence of two isomeric dimeric forms in solution each of which features two inequivalent ($^t$BuNCH) units for the DAB ligands. In other words, the ligand(s) do(es) not obey the potential symmetry of point groups $C_s$ or $C_{2v}$, and they are different in the two isomers, as are the Ga–H moieties.

Three isomers can be drawn for the compound, one of which (**B**) was confirmed for $[(^tBu_2DAB)AlCl]_2$ and for $[(^tBu_2DAB)$-$Ga^tBu]_2$ by X-ray diffraction.[10,13] Forms **B** *and* **C** were found for aluminium and gallium complexes with the *saturated* ligand ($NCH_2CH_2N$ instead of NCH=CHN loops in the ligand).[11,14] Form **D** has not yet been observed. Note that each of these forms (**B**–**D**) has two inequivalent ($^t$BuNCH) units but equivalent metal substituents (*e.g.* Ga–H). The NMR data of **2** would therefore be compatible with a mixture of two of these isomeric dimers in the stoichiometric ratio 1 : 1. Interconversion on the NMR time scale must be slow at room temperature.

**Table 1** Selected bond lengths (Å) and angles (°) of the structures **2**–**4**. For the disordered molecules of **2** the data are given only for one of the two components. For the four independent molecules of **3** data are given only for one representative example. A full set of data has been deposited

| | | | |
|---|---|---|---|
| **2** | | | |
| Ga1–H11 | 1.46(6) | N1–Ga–N1A | 86.35(12) |
| Ga1–N1 | 2.004(3) | Ga1–N1–Ga1A | 93.65(12) |
| Ga1–N1A | 2.021(3) | N1–Ga1–N2 | 90.44(18) |
| Ga1–N2 | 1.867(6) | N2–Ga1–N1A | 113.5(2) |
| N1–C1 | 1.473(5) | | |
| N2–C2 | 1.372(6) | | |
| C1–C2 | 1.331(6) | | |
| **3** | | | |
| Ga11–Cl12 | 2.171(2) | N13–Ga11–N11 | 89.3(2) |
| Ga11–Cl11 | 2.1731(19) | N13–Ga12–N11 | 86.0(2) |
| Ga11–N13 | 1.979(5) | Ga11–N11–Ga12 | 92.1(2) |
| Ga11–N11 | 1.979(5) | Ga11–N13–Ga12 | 92.6(2) |
| Ga12–N11 | 2.047(5) | Cl12–Ga11–Cl11 | 104.80(9) |
| Ga12–N13 | 2.031(5) | N14–Ga12–N13 | 92.2(2) |
| Ga12–N12 | 1.857(5) | N12–Ga12–N11 | 91.7(2) |
| Ga12–N14 | 1.846(5) | N12–Ga12–N13 | 118.2(2) |
| | | N14–Ga12–N11 | 119.2(2) |
| **4** | | | |
| Ga–Cl | 2.1554(8) | N1–Ga–N1A | 87.76(8) |
| Ga–N1 | 2.0169(19) | Ga–N1–GaA | 92.24(8) |
| Ga–N1A | 1.9860(18) | N1–Ga–N2 | 90.44(18) |
| Ga–N2 | 1.8633(18) | N2–Ga–N1A | 118.68(8) |
| N1–C1 | 1.466(3) | | |
| N2–C2 | 1.380(3) | | |
| C1–C2 | 1.341(3) | | |

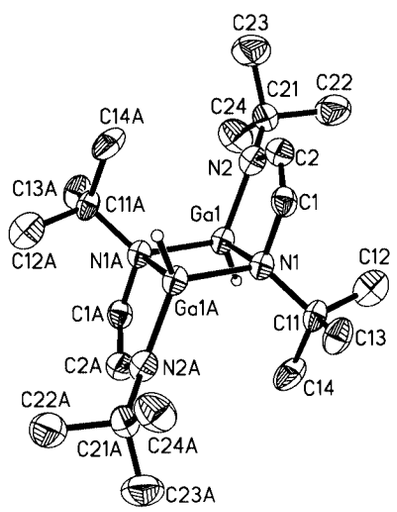


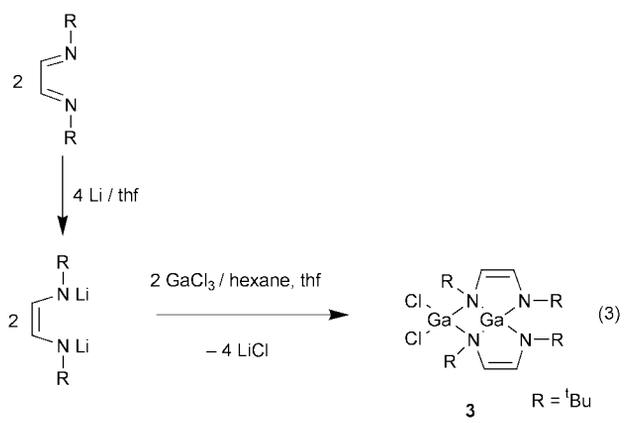

**Fig. 1** Molecular structure of $[(^tBu_2DAB)_2GaH]_2$ **2** with atomic numbering (ORTEP[16]). The molecules are disordered and only one of the two components is shown. The structure belongs to type **B** (Scheme 2) and has a crystallographic centre of inversion. For details see Table 1.

The single crystal X-ray structure analysis of the hydride **2** showed that the crystals grown from pentane at room temperature contain only form **B** (Fig. 1). The crystals are disordered, but the structure could be refined using a split model with two components. The structures of these two molecules are very similar and no separate discussion is necessary. The core unit of **2** is a four-membered ring $(Ga–N)_2$ with one hydrogen atom at each gallium atom in *trans* positions. Together with this four-membered ring, the two five-membered rings of the tricyclic compound represent a folded chair. The structural details (Table 1) are not unusual.

In summary it appears that the gallium hydride dimer **2** exists in solution in two isomeric forms which are in equilibrium with slow interconversion. Crystallization leads to the precipitation exclusively of the symmetrical *trans* form **B**. We presently have no means to decide if the other form in solution is the *cis* form **C** generated by a ring flip, or form **D** which is the product of a ligand redistribution shifting both hydrogen atoms to one of the two gallium centres. High-temperature NMR studies are precluded owing to the limited stability range of the compound(s). For technical reasons, Ga NMR spectroscopy was not available.

### *cis*-Ethene-1,2-di(*tert*-butylamido)gallium chloride 3

For the preparation of compound **3** anhydrous gallium trichloride was reacted with equimolar quantities of $Li_2{}^tBu_2DAB$ in tetrahydrofuran at room temperature [eqn. (3)].




Evaporation of the solvent and extraction of the residue with hexane gave the expected product in 80% yield as a light green solid. It is known from previous studies[15] that the light green colour originates from a radical species $[(^tBu_2DAB)_2Ga]$ which shows up even in traces owing to its strong absorption characteristics. Yellow single crystals of compound **3** could be grown from hexane at −28 °C. The composition was confirmed by elemental analysis and by the mass spectrum (CI) which showed the parent ion of the dimer.

It is worth noting that the reaction according to eqn. (3) was carried out previously, but different products were obtained, probably owing to partial hydrolysis.[12]

The $^1H$ and $\{^1H\}^{13}C$ NMR spectra of **3** (in benzene-$d_6$) show two sets of signals for the ($^t$BuNCH) units indicating that only one of the three isomeric dimers (**B**–**D**) is present in solution. Very unexpectedly, this isomer is a prototype of the new form **D** as shown by X-ray crystallography.

Crystals of compound **3** grown from pentane at −28 °C and investigated at −80 °C have a very large unit cell (monoclinic, space group $C2/c$, $V = 18468$ Å$^3$!) containing no less than 28 molecules. The asymmetric unit comprises seven monomers $(^tBu_2N_2(CH)_2)_2GaCl$, or three and a half dimers, one of which has crystallographically imposed $C_2$ symmetry. The twofold axis passes through the gallium atoms Ga41 and Ga42 (Fig. 2).

The dimensions of all four dimers are very similar. The molecules belong to the isomer type **D** with *in*equivalent gallium atoms. (Note that the gallium atoms in both **B** and **C** are equivalent.) Upon dimerization the chlorine atom of one monomer is transferred to the gallium atom of the other monomer such that the first gallium atom is finally tetracoordinated by four nitrogen atoms while the other one bears two nitrogen and two chlorine atoms. (In forms **B** and **C** all gallium atoms are coordinated to three nitrogen atoms and one chlorine atom.)

The molecules of **3** thus have a different tricyclic structure as compared to **B** and **C**: The five-membered rings are attached to

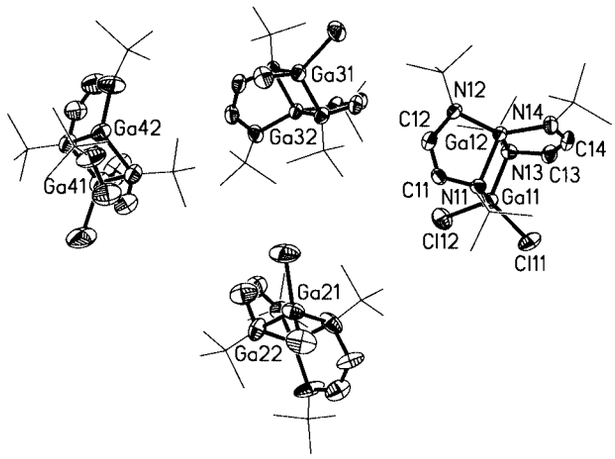


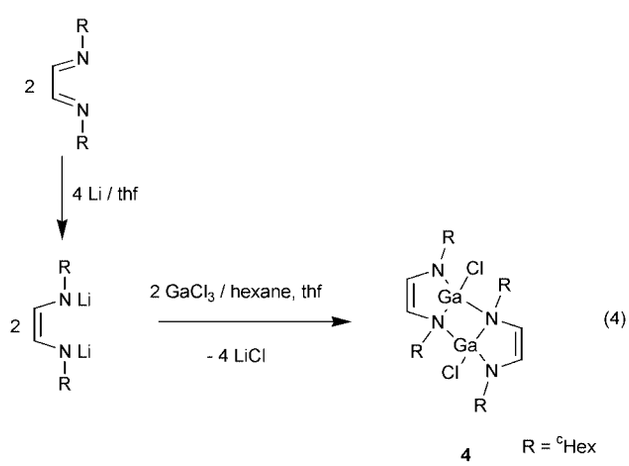

**Fig. 2** Molecular structure of $[(^tBu_2DAB)GaCl]_2$ **3** with atomic numbering (ORTEP[16]). The asymmetric unit contains three and one half of the dimers, which belong to type **D** (Scheme 2). The fourth dimer is generated from the monomer by the crystallographic twofold axis passing through the two gallium atoms (Ga41, Ga42). The structures of the four dimers are very similar and therefore details are only listed for one representative example in Table 1.

*neighbouring* edges of the four-membered ring core $(Ga–N)_2$, while in **B** and **C** the five-membered rings are attached to *opposite* edges of this central unit.

The Ga–N distances of the gallium atoms in **3** bearing the two chlorine atoms are generally significantly shorter than the remaining two Ga–N bonds of the four-membered ring. All three rings (four- and five-membered) are virtually planar. Since all four molecules in the asymmetric unit have the same structure, and since there are no unusual intermolecular contacts, it is unlikely that the isomeric form **D** is determined by packing forces. It is more probable that steric effects of the bulky *tert*-butyl groups and the larger size of the chlorine atom (as compared to the hydrogen atom in the above hydride **2**) cause a ligand redistribution. This assumption suggested complementary investigations of a compound with substituents of reduced steric bulk.

### *cis*-Ethene-1,2-di(cyclohexylamido)gallium chloride 4

The reaction of anhydrous gallium trichloride with $Li_2{}^tBu_2$-DAB was carried out as described for the *tert*-butyl analogue above [eqn. (4)].




The product **4** was obtained in 72% yield as a pale red solid. Colourless single crystals could be grown from hexane at −28 °C. The composition was confirmed by the mass spectrum (CI: $m/z = 648$) and by the $^1H$ and $\{^1H\}^{13}C$ NMR spectra, which showed two sets of signals for the $[(^cHexNCH)_2]$ groups.

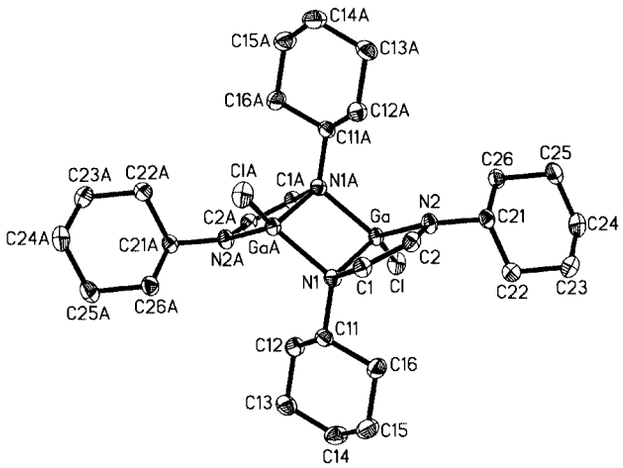



**Fig. 3** Molecular structure of $[(^{c}Hex_2DAB)GaCl]_2$ **4** with atomic numbering (ORTEP[16]). The molecule has a crystallographic centre of inversion in the middle of the $(Ga–N)_2$ four-membered ring and belongs to the structure type **B** (Scheme 2). For details see Table 1.

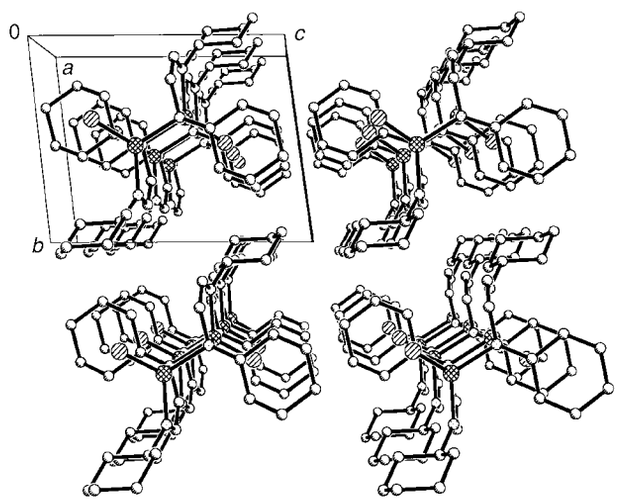



**Fig. 4** Molecular packing in the crystal lattice of compound **4** (projection along the *a* axis).

Crystals of the cyclohexyl compound **4** are triclinic, space group $P\bar{1}$, with one formula unit in the unit cell. This molecule has a crystallographically imposed centre of inversion in the middle of the $(Ga–N)_2$ four-membered ring (Fig. 3). The structure thus corresponds to the dimer type **B** and is similar to the structure of the above hydride **2**. In the lattice there are no conspicuous sub-van der Waals contacts between neighbouring molecules (Fig. 4). The change of the structure type on going from the example with *tert*-butyl substituents (**3**) to the example with cyclohexyl substituents (**4**) is therefore most likely due to the reduced steric bulk of the organic groups.

In summary our results have shown that the structural chemistry of (diazabutadiene)gallium hydrides and halides may be rather complex. The assignment of spectral and other analytical data as well as any predictions regarding the structure of an individual compound of this series need to be made with great scrutiny and care. Our studies of synthetic pathways to the initial targets (formula **A** above) will be continued.

## Experimental

All experiments were routinely carried out in a glove-box filled with purified argon. Transfer of samples was executed in a nitrogen atmosphere using standard Schlenk apparatus. Conventional equipment was used for analytical and spectroscopic measurements. The starting materials ($GaCl_3$, $Et_3SiH$, lithium metal) were commercially available, $^{t}Bu_2DAB$ and $^{c}Hex_2DAB$ were prepared according to a literature procedure.[17] Solvents were rigorously dried and saturated with argon or nitrogen, and glassware was oven-dried and filled with argon or nitrogen.

### $[GaHCl_2]_2$ 1

Anhydrous gallium trichloride (8.8 g, 50 mmol) and triethylsilane (7.99 g, 51 mmol) were combined at −13 °C and stirred for 1 h. The reaction mixture was allowed to warm to 0 °C and the formed triethylchlorosilane evaporated. The remaining product (100% yield) was recrystallized from hexane at −78 °C to give a white microcrystalline solid which decomposed slowly at room temperature (60% yield). $^1$H NMR ($d_8$-toluene, 0 °C): $\delta$ 5.51 (br s).

### $[(^{t}Bu_2N_2(CH)_2)GaH]_2$ 2

A solution of 1,4-dilithio-1,4-di-*tert*-butyl-1,4-diazabutadiene in tetrahydrofuran (40 mL) was prepared from the diazabutadiene (3.18 g, 18.92 mmol) and lithium metal (0.26 g, 37.84 mmol) and treated with a solution of dichlorogallane (2.68 g, 18.92 mmol) in tetrahydrofuran (20 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature overnight, the solvent evaporated and the residue extracted with pentane (50 mL). The solvent was again evaporated to leave a light yellow solid (78% yield). The product sublimed at 100 °C and $3 \times 10^{-1}$ mbar. Single crystals were grown from pentane solution at room temperature (Found: C, 50.96; H, 8.95; N, 12.18. $C_{20}H_{42}Ga_2N_4$ requires C, 50.25; H, 8.86; N, 11.72%). IR ($cm^{-1}$): 1917.7s, 1927.1s. $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 6.46 (dd, 2 H, $^3J_{HH}$ = 4.0, $^4J_{HH}$ = 2.9, =CH), 6.38 (dd, 2 H, $^3J_{HH}$ = 4.0, $^4J_{HH}$ = 2.1, =CH), 6.19 (br s, 2 H, Ga-H), 5.67 (br s, 2 H, Ga-H), 5.15 (dd, 2 H, $^3J_{HH}$ = 4.4, $^4J_{HH}$ = 1.5, =CH), 4.65 (dd, 2 H, $^3J_{HH}$ = 4.4, $^4J_{HH}$ = 1.1 Hz, =CH), 1.28 (s, 18 H, $C(CH_3)_3$), 1.23 (s, two coinciding resonances 36 H, $C(CH_3)_3$), 1.21 (s, 18 H, $C(CH_3)_3$). $^{13}$C-{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 136.10 (s, =CH), 134.56 (s, =CH), 105.46 (s, =CH), 104.02 (s, =CH), 56.35 (s, C–N), 56.06 (s, C–N), 52.57 (s, C–N), 51.47 (s, C–N), 31.73 (s, $C(CH_3)_3$), 31.69 (s, $C(CH_3)_3$), 28.15 (s, $C(CH_3)_3$), 27.86 (s, $C(CH_3)_3$). MS (CI): *m*/*z* 476 $[(^{t}Bu_2N_2(CH)_2)GaH]_2^+$.

### $[(^{t}Bu_2N_2(CH)_2)GaCl]_2$ 3

A solution of 1,4-dilithio-1,4-di-*tert*-butyl-1,4-diazabutadiene in tetrahydrofuran (15 mL) was prepared from the diazabutadiene (1.68 g, 10 mmol) and lithium metal (0.139 g, 10 mmol) and treated with a solution of anhydrous gallium trichloride (1.76 g, 10 mmol) in hexane (15 mL). The solvent was evaporated and the residue extracted with hexane (20 mL). The solvent was again evaporated to leave a light green solid (80% yield). Single crystals were grown from hexane solutions at −28 °C: mp 141 °C (decomp.) (Found: C, 43.98; H, 7.80; N, 10.25. $C_{20}H_{40}Cl_2Ga_2N_4$ requires C, 43.92; H, 7.37; N, 10.25%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 6.35 (d, 2 H, $^3J_{HH}$ = 4.62, =CH), 5.23 (d, 2 H, $^3J_{HH}$ = 4.62 Hz, =CH), 1.32 (s, 18 H, $^{t}$Bu), 1.12 (s, 18 H, $^{t}$Bu). $^{13}$C-{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 135.1 and 104.9 (s, =CH), 58.6 and 53.0 (s, $C(CH_3)_3$), 31.7 and 28.1 (s, $C(CH_3)_3$). MS (CI): *m*/*z* 541 $[(^{t}Bu_2N_2(CH)_2)GaH]_2^+$.

### $[(^{c}Hex_2N_2(CH)_2)GaCl]_2$ 4

A solution of 1,4-dilithio-1,4-dicyclohexyl-1,4-diazabutadiene in tetrahydrofuran (15 mL) was prepared from the diazabutadiene (2.20 g, 10 mmol) and lithium metal (0.139 g, 20 mmol) and treated with a solution of anhydrous gallium trichloride (1.76 g, 10 mmol) in hexane (15 mL). The solvent was evaporated and the residue extracted with hexane (20 mL). The solvent was again evaporated to leave a red solid (72% yield). Colourless single crystals were grown from hexane solution at −28 °C. $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 6.37 (d, 2 H, $^3J_{HH}$ = 6.96, =CH), 5.18 (d, 2 H, $^3J_{HH}$ = 6.96 Hz, =CH), 3.29 (m, 2 H, $H_{ipso}$), 2.98 (m, 2 H, $H_{ipso}$), 2.20–0.86 (m, 44 H, $CH_2$). $^{13}$C-{$^1$H} NMR ($C_6D_6$, 20 °C):

**Table 2** Crystal data, data collection and structure refinement for compounds **2**–**4**

| | **2** | **3** | **4** |
|---|---|---|---|
| Empirical formula | $C_{20}H_{42}Ga_2N_4$ | $C_{20}H_{40}Cl_2Ga_2N_4$ | $C_{28}H_{48}Cl_2Ga_2N_4$ |
| $M$ | 478.02 | 546.90 | 651.04 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $C2/c$ | $P\bar{1}$ |
| $a$/Å | 10.077(2) | 61.445(13) | 8.140(2) |
| $b$/Å | 9.818(1) | 10.441(1) | 8.639(2) |
| $c$/Å | 12.304(2) | 29.371(10) | 10.674(2) |
| $\alpha$/° | 90 | 90 | 82.15(2) |
| $\beta$/° | 100.16(1) | 101.45(1) | 89.32(2) |
| $\gamma$/° | 90 | 90 | 81.16(2) |
| $V$/Å$^3$ | 1198.2(3) | 18468(8) | 734.7(3) |
| $Z$ | 2 | 28 | 1 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 22.6 | 22.6 | 20.40 |
| $T$/K | 143 | 193 | 166 |
| Measured reflections | 4436 | 16523 | 3177 |
| Unique reflections ($R_{int}$) | 2580 (0.0259) | 16188 (0.0288) | 3177 |
| Reflections [$I > 2\sigma(I)$] | 2580 | 16188 | 3177 |
| Refined parameters | 243 | 911 | 259 |
| $R1$ [a] [$I > 2\sigma(I)$] | 0.0301 | 0.0615 | 0.0295 |
| $wR2$ [b] | 0.0710 | 0.1286 | 0.0741 |
| Weighting scheme [b] | $a = 0.0390$ | $a = 0.0464$ | $a = 0.0545$ |
| | $b = 0.22$ | $b = 152.30$ | $b = 0.21$ |
| $\sigma$(max./min.)/e Å$^{-3}$ | 1.004/−1.560 | 1.300/−0.887 | 0.769/−1.078 |

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

$\delta$ 138.8 (s, =CH), 102.6 (s, =CH), 60.0–25.0 (m, $C_6H_{11}$). MS (CI): $m/z$ 648 [($^c$Hex$_2$N$_2$(CH)$_2$)GaCl]$_2^+$.

### Crystal structure determinations

Specimens of suitable quality and size of compounds **2**, **3** and **4** were used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer [Mo-K$\alpha$ radiation, $\lambda$(Mo-K$\alpha$) = 0.71073 Å]. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. $L_p$ correction was applied but intensity data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS-86 [18]) and completed by full-matrix least squares techniques against $F^2$ (SHELXL-93 [19]). The structure of compound **2** suffered from disorder and was refined in split positions, with restraints concerning the C–C bonds of the $^t$Bu groups as well as N–C($^t$Bu) bonds. The thermal motion of all non-hydrogen atoms was treated anisotropically. All C–H atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.2 \times U_{eq}$ of the attached C atom). The Ga–H atoms of compound **2** were located and included in the refinement with isotropic contributions.

Further information on crystal data, data collection and structure refinement is summarized in Table 2. Important interatomic distances and angles are shown in Table 1.

CCDC reference number 186/1856.

See http://www.rsc.org/suppdata/dt/a9/a909198j/ for crystallographic files in .cif format.

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