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Synthesis, structure and reactions of an amidinate stabilised trigallane[†]‡

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The neutral trigallane $R_3Ga_3I_2$ was obtained in high yields by reaction of "GaI" with the moderately sterically demanding lithium N,N'-dicyclohexylneopentylamidinate. Its chemical reactions with N-lithio-2-propanimine, sodium superhydride and elemental iodine were investigated. RI-DFT calculations have been performed to confirm the bonding situation. All compounds are characterised by crystal structure analysis and NMR-spectroscopy.

Introduction 1

Low-valent gallium compounds have been of wide interest in the last few years. Mostly, these compounds form clusters, cages or rings.¹⁻⁴ There are only a few examples of open gallium chains. A large variety of digallanes(4) of type Ga_2R_4 have been prepared with various substituents ranging from alkyl-5 and aryl groups⁶ to silyl-,⁷ amino-⁸ and alkoxy groups.⁹ With Lewis-basic substituents oligomerisation is possible. For example, $[(Me_3Si)_3SiGaCl]_4{}^7$ and $({^\prime}BuO)_8Ga_4{}^9$ with digallane units in cage molecules have been synthesized. By reaction of "GaI" and triethylphosphane [PEt₃GaI₂-GaIPEt₃-GaI₂PEt₃]¹⁰ was obtained. We isolated the linear, anionic [(Ph₃Ge)₃Ga–Ga–Ga(GePh₃)₃]⁻ as a product from the reaction of Li(thf)₃GePh₃ with "GaI".¹¹ Less highly substituted trigallanes form rings like $[Aryl_3Ga_3]^{2-12}$ (Aryl= 2,6-dimesitylphenyl) and ('Bu₃Si)₄Ga₃.¹³ Curing the electron deficiency by incorporating donors into the substituent leads to alkane-like chains with gallium-gallium-bonds: From the reaction of the anionic heterocyclic compound [{CHNdipp}₂Ga]⁻¹⁴ with GaH_3 ·quinuclidine the trigallanate [{CHNdipp}₂Ga-GaH₂-Ga{CHNdipp}₂]⁻¹⁵ could be isolated, which is bent, due to tetrahedral coordination at the central gallium atom (dipp = 2,6diisopropylphenyl). [(nacnac)ClGa-GaCl-GaCl(nacnac)] and [(nacnac)MeGa-GaMe-GaMe(nacnac)]16 were obtained by oxidative addition reactions of GaCl₃ and GaMe₃ to Ga(nacnac)¹⁷ $(nacnac = HC{C(Me)N(dipp)}_2)$. Using the structurally related guanidinate instead of amidinate it has been possible to isolate a gallium(I) species, the $[Ga(\{dippN\}_2CNCy_2)]^{18}$ (Cy = cyclohexyl). This has been shown to react with complex fragments of platinum, iron, cobalt, nickel and molybdenum as a CO-analog.¹⁹⁻²¹ Amidinates are valuable substituents in main group and transition

metal chemistry, as well.²² Using an amidinate substituent a germanium(I) compound with a Ge-Ge-bond (GeAmCl)₂ has been synthesized.²³ The bis(alkylamidinate) Group 4 metal complexes of the general formula $[RC(NCy)_2]_2MCl_2$ (M = Ti, Zr, Hf; R = Me, ^tBu) are active ethylene polymerization catalysts in the presence of methylaluminoxane (MAO) as a cocatalyst.24

Here we examine the reactions of chelating amidinates with galliumsubiodide resulting in corresponding functional digallane and trigallane compounds. Using a moderately sterically demanding lithium amidinate provides a chain, composed of three gallium atoms - stabilised by three amidinate residues, shielding the central gallium atom - and two terminal iodine atoms, in excellent yields (>80%). These iodine atoms are perfect groups for further metathesis reactions. These have been performed by adding lithium propan-2-ylideneamide or sodium superhydride, respectively.

2 **Experimental**

All procedures were performed under purified argon or in vacuum using Schlenk techniques. Starting materials were prepared according to literature or used as purchased. Elemental analyses were done in the microanalytical laboratory of the Institute of Inorganic Chemistry, University of Heidelberg, Heidelberg, Germany. NMR spectra were recorded on a BRUKER DRX200, a Bruker Advance II 400 or a BRUKER AVANCE III 600 instrument. X-ray crystallography: suitable crystals were mounted with perfluorinated polyether oil on the tip of a glass fibre and cooled down to 200 K immediately on the goniometer head. Data collection was performed on a STOE IPDS I diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Structures were solved and refined with the Bruker AXS SHELXTL 5.1 program package.25 Refinement was in full matrix against F^2 . All carbon-bonded hydrogen atoms were included as riding models with fixed isotropic U values in the final refinement. Due to the quality of the crystals of 4 the NCMe₂-group had to be treated with restraints (DELU, DFIX C52 C54). In all structures the largest remaining peaks are located near a heavy atom (I or Ga).

Weighting scheme:

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where

$$P = \frac{1}{3}(F_o^2 + 2F_c^2)$$

For further data, refer to Table 1.

2. 3.63 g (10 of bis-2.6-Synthesis of mmol) diisopropylphenylcarbodiimide were dissolved in 20 mL diethyl ether and cooled to 0 °C. 6.5 mL methyl lithium solution (5% in diethyl ether) were added. After overnight stirring, all volatiles were removed in vacuum. The residue 1a was suspended in toluene and added to 20 mmol "GaI" in toluene at -78 °C. After overnight stirring, the solution had darkened and elemental gallium had precipitated. All volatiles were removed in vacuum. The residue was extracted with thf. Upon cooling to -20 °C this solution yielded colourless crystals of 2. Yield: 2.00 g (35%); m.p. >240 °C (dec.).

2: $C_{52}H_{74}Ga_2I_2N_4$ (1148.4 g mol⁻¹) calcd. C 54.38, H 6.49, Ga 12.14, I 22.10, N 4.88, found C 54.64, H 6.58, N 4.99. ¹H-NMR (400 MHz, C_6D_6): δ [ppm] = 1.07 (d, 24 H, ${}^3J_{H-H}$ = 6.9 Hz, CH*Me*), 1.21 (d, 24 H, ${}^3J_{H-H}$ = 6.9 Hz, CH*Me*), 1.91 (s, 6 H, N–C(*Me*)=N), 3.23 (sept, ${}^3J_{H-H}$ = 6.9 Hz, 8 H, *CH*Me₂), 6.95 (d, ${}^3J_{H-H}$ = 7.7 Hz, 8 H, *m*-Ar–H), 7.09 (t, ${}^3J_{H-H}$ = 7.7 Hz, 4 H, *p*-Ar–H). ¹³C-NMR

Table 1 Crystallographic data of 2, 3, 4, 5 and 6

(600 MHz, C_6D_6): δ = 14.8 (N–C(*Me*)=N), 22.7 (CH*Me*), 24.9 (CH*Me*), 29.1 (*C*HMe₂), 124.6 (*m*-Ar–C), 129.9 (*p*-Ar–C), 146.0 (*i*-Ar–C), (N*C*N and *o*-Ar–C n.o).

Synthesis of 3. In a typical experiment 2.06 g (10 mmol) of dicyclohexylcarbodiimide were dissolved in 20 mL diethyl ether and cooled to 0 °C. 6.8 mL tert-butyl lithium solution (15% in n-hexane) were added. Almost immediately the liquid turned into a gel. After overnight stirring a white suspension was obtained. All volatiles were removed in vacuum. The resulting 1b was suspended in toluene and added to 16.7 mmol "GaI" in toluene at -78 °C. After overnight stirring, the solution darkened and elemental gallium precipitated. All volatiles were removed in vacuum. The residue was first extracted with n-hexane, then with toluene and finally with thf. The n-hexane-fraction yielded crystals of 3a (3.nhexane), the toluene-fraction yielded crystals of 3b (3-toluene) and the thf-fraction yielded crystals of 3c (3.thf). Depending on temperature and concentration solvent free 3 could be obtained from the toluene-fraction. The total yield of trigallane 3 was 3.43 g $(82\%), m.p. > 330 \circ C (dec).$

3: $C_{51}H_{93}Ga_3I_2N_6$ (1253.3 g mol⁻¹) calcd. C 48.87, H 7.48, N 6.71, Ga 16.69, I 20.25, found C 49.35, H 7.37, N 6.10. ¹H-NMR (200 MHz, C_6D_6): δ [ppm] = 1.08–1.86 (m, 60 H, ^chex), 1.20 (s, 9 H, N–C(–CMe₃)=N), 1.21 (s, 9 H, N–C(–CMe₃)=N), 1.27 (s, 9 H, N–C(–CMe₃)=N), 3.75 (m, 6 H, *i*-H ^chex). ¹³C-NMR (400 MHz, C_6D_6): δ = 25.3–25.9 (^chex, *m*-*C*), 26.7–26.8 (^chex, *p*-*C*), 29.4–30.0

Compound	2	3	4	5	6
Empirical formula	C ₂₆ H ₃₇ GaIN ₂	$C_{51}H_{93}Ga_3I_2N_6$	C ₆₆ H ₁₂₃ Ga ₃ IN ₇ O ₃	C ₅₃ H ₉₉ Ga ₃ N ₆	$C_{17}H_{31}GaI_2N_2$
Formula weight/g mol ⁻¹	574.20	1253.27	1398.77	1029.54	586.96
Crystal size/mm	$0.33 \times 0.22 \times 0.19$	$0.44 \times 0.35 \times 0.08$	$0.26 \times 0.20 \times 0.09$	$0.27 \times 0.26 \times 0.16$	$0.45 \times 0.18 \times 0.16$
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P 2_1/c$	PĪ	Cc	$P 2_1/c$	C 2/c
a/Å	10.364(2)	12.293(3)	13.184(3)	12.634(3)	27.952(6)
b/Å	17.629(4)	13.507(3)	30.314(6)	20.821(4)	10.316(2)
c/Å	15.399(3)	18.197(4)	17.950(4)	21.296(4)	17.640(4)
$\alpha /^{\circ}$	90.00	81.06(3)	90.00	90.00	90.00
β/°	107.90(3)	77.42(3)	95.17(3)	90.57(3)	123.05(3)
γ/°	90.00	69.29(3)	90.00	90.00	90.00
$V/Å^3$	2677.3(9)	2748.2(10)	7145(2)	5601.7(19)	4263.4(15)
Ζ	4	2	4	4	8
$D_{\rm calc}/{\rm g~cm^{-3}}$	1.425	1.515	1.300	1.221	1.829
μ (Mo-K α)/mm ⁻¹	2.195	2.622	1.601	1.470	4.187
Absorption correction	Numerical	Numerical	Numerical	Numerical	Numerical
$T_{\rm min}/T_{\rm max}$	0.5928/0.6829	0.3697/0.7698	0.5012/0.8727	0.7026/0.8234	0.2492/0.5350
<i>F</i> (000)/e	1164	1280	2952	2208	2272
$\theta/^{\circ}$	2.3726.07	2.3028.16	1.7624.26	2.4928.17	2.2928.00
Index ranges	$-12 \le h \le 12$	$-16 \le h \le 16$	$-15 \le h \le 15$	$-16 \le h \le 16$	$-36 \le h \le 36$
	$-21 \le k \le 21$	$-17 \le k \le 17$	$-34 \le k \le 33$	$-27 \le k \le 27$	$-13 \le k \le 13$
	$-19 \le 1 \le 18$	$-23 \le 1 \le 23$	$-20 \le 1 \le 20$	$-27 \le l \le 27$	$-23 \le 1 \le 22$
Reflections collected	21208	26791	23360	54075	20006
Independent reflections	5269	12307	10854	13382	5052
Observed refl. $[I > 2\sigma(I)]$	3806	5380	4701	4061	3457
Completeness of data	$\theta = 26.07^{\circ}; 99.4\%$	$\theta = 28.16^{\circ}; 91.2\%$	$\theta = 24.26^{\circ}; 98.6\%$	$\theta = 28.17^{\circ}; 97.3\%$	$\theta = 28.00^{\circ}; 98.1\%$
Data/restraints/parameters	5269/0/271	12307/0/559	10854/40/721	13382/0/563	5052/0/199
Goodness of fit (S) on F^2	0.880	0.656	0.769	0.780	0.937
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.0295	0.0362	0.0676	0.0611	0.0432
	0.0621	0.0672	0.1358	0.1179	0.1044
R indices (all data)	0.0466	0.1079	0.1440	0.1995	0.0668
<u>,</u>	0.0650	0.0765	0.1640	0.1617	0.1122
Max diff. peak/hole [e Å ⁻³]	0.531/-0.392	0.946/-0.878	1.612/-0.845	0.688/-0.555	1.159/-1.101
w_1	0.0355	0.0232	0.0324	0.0491	0.0572
CCDC reference number	811974	811976	811980	811981	811982

(CMe₃), 35.1–36.2 (^chex, *o*-*C*), 38.6–39.9 (*C*Me₃), 53.7–55.8 (^chex, *i*-*C*), 175.1 (N–*C*(-CMe₃)=N).

Synthesis of 4. 2 mL (3 mmol) of a methyl lithium solution (5 w% in diethyl ether) were added to 10 mL of acetonitrile. A white precipitate formed. All volatiles were removed in vacuum and the precipitate was dissolved in thf. At -78 °C this solution was added to 3.80 g (3 mmol) of **3** in toluene. After overnight stirring all volatiles were removed in vacuum. The residue was extracted with thf. This solution yielded some colourless crystals of **4** which were used for X-ray diffraction and NMR, m.p. > 260 °C (dec.).

4: ¹H-NMR (600 MHz, C_6D_6): δ [ppm] = 1.00–1.97 (m, 87 H, ^chex, ^{*i*}Bu), 2.00–2.22 (m, N=CMe₂), 3.77 (m, 6 H, *i*-H^chex). ¹³C-NMR (600 MHz, C_6D_6): δ [ppm] = 25.5–26.4 (^chex, *m*-C, *p*-C), 28.7 (N=CMe₂), 29.1 (N=CMe₂), 29.2–29.6 (CMe₃), 34.8–35.9 (^chex, *o*-C), 38.6–39.5 (CMe₃), 53.4–55.8 (^chex, *i*-C), 159.5 (N=CMe₂).

Synthesis of 5. 4.5 mL (4.5 mmol) of a solution of Na[BEt₃H] ($c = 1 \text{ mol } l^{-1}$) in toluene were added at $-78 \text{ }^{\circ}\text{C}$ into a solution of 2.82 g (2.25 mmol) of **3** in 20 mL toluene. After stirring for an hour the solution turned yellowish. After further overnight stirring all volatiles were removed in vacuum. The residue was extracted with n-hexane. This solution yielded colourless crystals of **5** upon cooling to $-20 \text{ }^{\circ}\text{C}$.

5: ¹**H-NMR** (400 MHz, CDCl₃): δ [ppm] = 0.90–1.75 (m, 92 H, *chex*, *'Bu*, *Et*), 5.28 (m, ³J_{*H*-*H*} = 1.01 Hz, 6 H, *i*-*H* ^chex), 5.4 (s, 1 H, Ga*H*, broad peak).- ¹³**C-NMR** (400 MHz, CDCl₃): δ = 7.7 (CH₂CH₃), 17.4 (CMe₃), 21.4 (CH₂CH₃), 25.6–25.7 (*m*-*C*, *p*-*C* ^chex), 29.2–29.9 (CMe₃), 36.6–36.9 (*o*-*C* ^chex), 54.1–54.7 (*i*-*C* ^chex), 175.1 (N–*C*('Bu)=N). **IR** (liquid cell, in n-hexane): \tilde{v} = 1755 cm⁻¹ (terminal Ga–H).

Synthesis of 6. A solution of 1.25 g (1 mmol) of 3 in 20 mL toluene was titrated with 20 mL of a 0.1 M iodine standard solution in toluene. During the titration the solution discolours immediately. An additional drop of iodine solution is not discoloured. The concentrated solution yielded colourless crystals of 6 upon cooling to -20 °C.

6: ¹**H-NMR** (200 MHz, C₆D₆): δ [ppm] = 1.15–1.78 (m, 20 H, ^{*c*}hex), 1.07 (s, 9 H, N–C(-CM*e*₃)=N), 3.66 (m, 2 H, *i*-H ^{*c*}hex).

3 Results and discussion

3.1 Synthesis

Lithium amidinates are obtained by the reaction of suitable carbodiimides with methyl lithium or *tert*-butyl lithium (eqn (1)). Reaction of "GaI"²⁶ with **1a** (eqn (2)) yields the functional diiodobis(amidinato)digallane **2**. In 2006 Jones *et al.*²⁷ reported the structures of di-iodo-bis(N,N'-bis(2,6-diisopropylphenyl)midoformamido)-di-gallium(II) and diiodo-bis(N,N'-bis(2,6-diisopropylphenyl)neopentylamidinato)-di-gallium(II) as the products of the reaction of "GaI" and lithium-N,N'-bis(2,6-diisopropylphenyl) neopentylamidinate and lithium-N,N'-bis(2,6-diisopropylphenyl)formamidinate, respectively. This shows that the alkyl group linking the nitrogen atoms has little effect on the structure.



Reducing the steric demand of the amidinato group by using dicyclohexylamidinates the trigallane 3 is obtained (eqn (3)) in good yield.



It has been demonstrated that in the functional digallane $[(Me_3Si)_3SiGaCl]_4^7$ attempted substitution reactions resulted in cleavage of the gallium–gallium bond. In order, to examine the stability of the shielded trigallium unit of **3** substitution reactions of the terminal iodo atoms were performed. By metathesis reaction of **3** with *N*-lithio-2-propanimine the mono substituted **4** is obtained, by preserving the trigallane unit (eqn (4)). The second iodine atom could not be exchanged, probably due to steric inhibition.



When reacting **3** with sodium triethylhydridoboranate, the first gallium(II)hydride **5** is obtained. One of the iodine atoms in **3** was substituted by a hydride, the other one by an ethyl group (eqn (5)). Obviously, the hydridoboranate is an alkylating reagent, too, in this case. ¹¹B-NMR of the reaction solution indicates the formation of Et_2BI among other products.²⁸



The reaction of **3** with elemental iodine in toluene at room temperature occurs immediately. It yields the gallium(III) compound **6** (eqn (6)). That allows a redox titration with an iodine standard solution in toluene. The consumption of iodine solution corresponds with a four electron reaction. This matches with the presence of two gallium(II) and one gallium(I) in **3**.



3.2 Spectroscopic characterization

The ¹H-NMR-spectrum of **2** shows two doublets ($\delta = 1.07$ (24 H) and $\delta = 1.21$ (24 H)) and one septet ($\delta = 3.23$ (8 H)) for the *iso*-propyl groups which is the usual pattern. The methyl group inside the amidinate creates a singlet at $\delta = 1.91$ (6 H). The aromatic hydrogen atoms are found at $\delta = 6.95$ (d, 8 H, *meta*) and $\delta = 7.09$ (t, 4 H, *para*).

The ¹³C-NMR-spectrum of **2** also shows for the *iso*-propyl groups two signals for the methyl groups at $\delta = 22.7$ and $\delta = 24.9$ and one signal for the methine group $\delta = 29.1$. The methyl carbon atoms inside the amidinate show up at $\delta = 14.8$. The aromatic *meta-*, *para-* and *ipso*-carbon atoms are found at $\delta = 124.6$, $\delta = 129.9$ and $\delta = 146.0$. The quaternary carbon atoms NCN and *ortho*-C could not be observed.

¹H-NMR- and ¹³C-NMR-spectra of **2** are consistent with a structure with an asymmetrical substituted gallium and 2/m symmetry.

The ¹H-NMR-spectrum of **3** shows a broad multiplet at $\delta = 1.08-1.86$ that corresponds with the 60 hydrogen atoms of the secondary carbon atoms in the cyclohexyl groups. The *tert*-butyl groups are found as three singlets at $\delta = 1.20$, 1.21 and 1.27 (9 H each). The six hydrogen atoms in *ipso*-position in the cyclohexyl groups are found at $\delta = 3.75$ as a quintet.

The ¹³C-NMR-spectrum of **3** shows three signals for the carbon atoms in *meta*-position at $\delta = 25.3-25.9$, the carbon atoms in *para*-position at $\delta = 26.7-26.8$, the carbon atoms in *ortho*-position $\delta = 35.1-36.2$ and for the carbon atoms in *ipso*-position at $\delta =$ 53.7-55.8. The methyl groups of the *tert*-butyl groups show up as a group of three signals at $\delta = 29.4-30.0$. The three quaternary carbon atoms in the *tert*-butyl groups are found at $\delta = 38.6-39.9$. The quaternary carbon atoms in the N₂C-groups are at $\delta = 175.1$. Here only one signal could be observed, the other two were lost in noise.

The ¹H-NMR-spectrum of **4** shows a broad multiplet at $\delta = 1.00-1.97$ (87 H, 'Bu, CH₂ ^chex). The hydrogen atoms in the *ipso*-position in the cyclohexyl groups are found at $\delta = 3.77$ (q, 6 H). So

far this fits the ¹H-NMR-spectrum of **3**. In addition there are the signals of the methyl groups of the N=CMe₂-group at $\delta = 2.00$ and $\delta = 2.22$ which could be observed.

The ¹³C-NMR-spectrum of **4** complies with **3**, though the quaternary carbons in the N₂C-groups could not be observed. In addition there are clear signals for the N==CMe₂-substituent in terms of the methyl groups at $\delta = 28.7$ and $\delta = 29.1$ and the quaternary carbon at $\delta = 159.5$.

The ¹H-NMR-spectrum of **5** reveals a broad signal in the typical range²⁹ for gallium-bound hydrides at $\delta = 5.4$ (1 H). The broad multiplet at $\delta = 0.90-1.75$ is caused by the overlapping signals of the *tert*-butyl-, the ethyl- and the methylene groups in the cyclohexyl groups. The tertiary hydrogen atoms in the cyclohexyl groups are to be found at $\delta = 5.28$.

The ¹³C-NMR-spectrum of **5** shows the usual signals of **3**. Additionally signals for the gallium-bound ethyl group are found at $\delta = 7.7$ (CH₂CH₃) and $\delta = 21.4$ (CH₂CH₃).

The IR-spectrum (liquid cell in n-hexane) shows a terminal Ga–H vibration at $\tilde{v} = 1755 \text{ cm}^{-1}.^{29}$

In summary, ¹H-NMR- and ¹³C-NMR-spectra of **3**, **4** and **5** reveal three sets of signals, one for each amidinate and the respective substituents. This indicates that the Ga_3 -unit is not only stable in the solid state but also in solution.

The ¹H-NMR-spectrum of **6** shows a broad multiplet at $\delta = 1.15-1.78$ (20 H, CH₂ ^chex). The methyl groups of the *tert*-butyl group are found at $\delta = 1.07$ (s, 9 H). The methine hydrogen atoms in the cyclohexyl groups correspond to the quintet at $\delta = 3.66$. The spectrum matches, in general, the one from gallium-N,N'-dicyclohexylneopentylamidinate dichloride.³⁰

3.3 Crystal structure determination

2 is obtained as colourless monoclinic crystals, space group $P 2_1/c$ (Fig. 1). In the centrosymmetric molecule the amidinate substituents bind to each of the gallium atoms in a chelating mode. The bite angle is 66.5(1)° and the Ga–N distances are 1.978(2) Å (Ga1-N1) and 1.986(2) Å (Ga1-N2), respectively. Each gallium atom is bonded to an iodine atom with a distance of 2.533(1) Å (Ga1-I1). The gallium-gallium-bond measures 2.430(1) Å (Ga1–Ga1'). This is similar to the bond length in the bis(N,N'bis(2,6-diisopropylphenyl)neopentylamidinate stabilised digallane and in diiodo-bis(N,N'-bis(2,6-diisopropylphenyl)formamidinato)-di-gallium(II).²⁷ The methyl group attached to the NCN fragment has a typical C-C single bond distance of 1.483(4) Å. As expected the C–N bonds in the N₂CGa-ring are of the same length within standard deviation: 1.319(3) Å (N1–C1), 1.315(3) Å (N2-C1). This indicates delocalization over the NCN fragment, which has been confirmed by quantum chemical calculations (see below). The phenyl rings are rotated 75°-78° to the NCN-plane. The isopropyl groups point away from the amidinate group.

If 2 is crystallized from thf, colourless, triclinic crystals of 2a, space group $P\bar{I}$ are obtained, which contain two molecules thf together with 2 in the asymmetric unit. Due to these thf molecules the digallane gets slightly twisted (torsion angle I1–Ga1–Ga2–I2 –169.5(1)°; see the Quantum chemical calculations section, too). The remaining structure is not affected by the solvent molecules.

Solvent free 3 was obtained by crystallization from toluene as colourless triclinic plates, space group $P\bar{1}$ (Fig. 2). The core



Fig. 1 Crystal structure of 2. The thermal ellipsoids are given at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–N1 1.978(2), Ga1–N2 1.986(2), Ga1–Ga1' 2.430(1), Ga1–I1 2.533(1), N1–C1 1.319(3), N1–C3 1.420(3), N2–C1 1.315(3), N2–C15 1.414(3), C1–C2 1.483(4); N1–Ga1–N2 66.5(1), N1–Ga1–Ga1' 120.9(1), N2–Ga1–Ga1' 119.4(1), N1–Ga1–I1 107.7(1), N2–Ga1–I1 109.5(1), Ga1'–Ga1–I1 120.7(1), C1–N1–C3 123.9(2), C3–N1–Ga1 144.8(2), C1–N2–C15 126.9(2), C1–N2–Ga1 91.1(1), C15–N2–Ga1 141.6(2), N2–C1–N1 111.2(2).

of a molecule 3 consists of a chain of three gallium atoms with distances of 2.420(1) Å and 2.415(1) Å. The Ga-Ga-Ga angle at the central gallium atom is 122.2(1)°. Each gallium is bonded to a dicyclohexylneopentylamidinate by its nitrogen atoms (1.950(4) Å-1.978(4) Å). The Ga-N bonds of Ga(1) and Ga(3) are shorter by 0.02 Å compared to the central gallium atom's bond lengths. This is conforming to Bent's rule.^{31,32} The terminal gallium atoms in oxidation state +II complete their distorted tetrahedral coordination with one iodine, each. The Ga-I-distances (2.594(1) Å–2.565(1) Å) are in the typical range. The amidinate groups binding to them have the same bite angle as in 2 within the standard deviation (66.3(2)°). The NCN-angles deviate significantly from the ideal 120° for a triple coordinated carbon (NCN 107.5(4) $^{\circ}$ (avg)). This is in line with the acute NGaN angles in the planar four membered GaN₂C rings. The amidinate bonded to the central Ga(2) (oxidation state +I) differs slightly, since the bite angle with $65.3(2)^{\circ}$ and the NCN-angle with $105.7(4)^{\circ}$ are a bit sharper, even.

We were able to obtain **3** cocrystallized with n-hexane (**3a**, colourless, triclinic crystals, space group $P\bar{I}$), toluene (**3b**, colourless, triclinic crystals, space group $P\bar{I}$) and thf (**3c**, colourless, monoclinic crystals, space group $P2_1/n$). The structures of **3a** and **3b** do not differ very much from **3**, but **3c** does. While the torsion angle I1–Ga1–Ga3–I2 in **3**, **3a** and **3b** is approximately 125–126°, in **3c** it is –88°. There is no close contact between the solvent molecules and the compound. A possible answer for this twist will be given in the Quantum chemical calculations section.

4 was obtained by crystallization from thf as colourless, monoclinic rods, space group Cc (Fig. 3). The unit cell contains three molecules of thf per molecule **4**. The Ga₃-unit forms an angle of 124.5(1)°, with distances of Ga(1)–Ga(2) 2.417(2) Å and Ga(2)–Ga(3) 2.436(2) Å. All gallium atoms are chelated by dicyclohexylneopentylamidinates, with Ga–N distances of 1.939(8) Å–1.984(7) Å and bite angles of 66.6(3)° (Ga(1)), 65.9(3)° (Ga(2)) and 68.2(3)° (Ga(3)). Ga(1) carries an iodine atom in



Fig. 2 Crystal structure of 3. The thermal ellipsoids are given at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: I1–Ga1 2.594(2), I2–Ga3 2.565(2), Ga1–N1 1.953(4), Ga1–N2 1.963(4), Ga1–Ga2 2.420(1), Ga2–N3 1.975(4), Ga2–N4 1.978(4), Ga2–Ga3 2.415(1), Ga3–N5 1.950(4), Ga3–N6 1.976(4); N1–Ga1–N2 66.0(2), N1–Ga1–Ga2 127.9(2), N2–Ga1–Ga2 127.9(2), N1–Ga1–I1 105.5(2), N2–Ga1–I1 107.1(2), Ga2–Ga3 112.7(1), N3–Ga2–Ga1 114.5(2), N4–Ga2–Ga3 114.0(2), N4–Ga2–Ga3 112.7(1), N3–Ga2–Ga1 114.5(2), N4–Ga2–Ga1 114.9(2), Ga3–Ga2–Ga1 122.2(1), N5–Ga3–N6 66.5(2), N5–Ga3–Ga2 125.7(2), N6–Ga3–Ga2 126.7(2), N5–Ga3–I2 109.1(1), N6–Ga3–I2 109.1(1), Ga2–Ga3–I2 112.1(1), C1–N1–Ga1 93.7(3), C1–N2–Ga1 93.0(3), C18–N3–Ga2 94.8(3), C18–N4–Ga2 94.1(3), C35–N5–Ga3 93.7(3), C35–N6–Ga3 92.0(3), N1–C1–N2 107.2(4), N3–C18–N4 105.7(4).

distorted tetrahedral coordination and typical distance (Ga(1)–I(1) 2.566(2) Å). The other Ga(II) in the molecule is bonded to an NCMe₂ group with a Ga(3)–N(7) distance of 2.02(1) Å and angles of 113.7(3)° (Ga(2)–Ga(3)–N(7)) and 115.0(4)° (C(35)–Ga(3)–N(7)). The Ga(3)–N(7)–C(52) unit is not linear (Ga(3)–N(7)–C(52) 133.9(10)°). It points away from the centre of the structure, in virtue of C(35)–Ga(3)–N(7)–C(52) 4(1)° and Ga(3)–N(7)–C(52)–C(53) 15(2)°.

5 was crystallized from n-hexane as colourless, monoclinic rods in space group $P 2_1/c$ (Fig. 4). Molecules of 5 contain a chain of three gallium atoms which form almost the same angle like in 3 (121.3(1)°). The Ga–Ga-distances are slightly elongated compared to 3 (Ga(1)–Ga(2) 2.457(2) Å and Ga(2)–Ga(3) 2.463(2) Å), which is in the line with Bent's rule.^{31,32} Each of the gallium atoms is chelated by one dicyclohexylneopentylamidinate, with Ga-Ndistances of 2.006(7) Å to 2.029(6) Å, which is slightly longer than in 3. Due to this elongation the bite angles have to decrease to $64.9(2)^{\circ}$ to $65.1(2)^{\circ}$. The distorted tetrahedral coordination sphere at Ga(1) at the one side of the chain is completed by a hydride (H(1)) (Ga(1)–H(1) 1.54(6) Å). Ga(3) at the other side of the chain is surrounded in a distorted tetrahedral manner by an amidinate, Ga(2) and an ethyl group (Ga(3)–C(52) 1.988(9) Å). This ethyl group points away from the molecule in a way, that the ethyl carbons, Ga(3) and the linking carbon of the amidinate rest are coplanar (torsion angle C(53)-C(52)-Ga(3)-C(35) -0.5(7)°).

6 was crystallized from toluene as colourless, monoclinic plates in space group C 2/c (Fig. 5). It is composed by a gallium atom in oxidation state +III distorted tetrahedral coordinated by two iodine atoms and chelated by one dicyclohexylneopentylamidinate (Ga(1)–I(1) 2.508(1) Å, Ga(1)–I(2) 2.491(1) Å, Ga(1)–N



Fig. 3 Crystal structure of 4. The thermal ellipsoids are given at the 50% probability level. Hydrogens and thf-molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–N1 1.939(8), Ga1–N2 1.981(9), Ga1–Ga2 2.417(2), Ga1–I1 2.567(2), Ga2–N3 1.958(8), Ga2–N4 1.984(7), Ga2–Ga3 2.436(2), Ga3–N5 1.947(8), Ga3–N6 1.974(8), Ga3–N7 2.02(1), C52–N7 1.14(2); N1–Ga1–N2 66.6(3), N1–Ga1–Ga2 125.0(2), N2–Ga1–Ga2 129.3(2), N1–Ga1–I1 107.1(2), N2–Ga1–I1 109.0(2), Ga2–Ga1–I1 111.7(1), N3–Ga2–N4 65.9(3), N3–Ga2–Ga3 114.5(2), Ga1–Ga2–Ga3 124.5(1), N5–Ga3–N6 68.2(3), N5–Ga3–N7 109.1(4), N6–Ga3–N7 109.7(4), N5–Ga3–Ga2 125.2(2), N6–Ga3–Ga2 122.9(2), N7–Ga3–Ga2 113.7(3), C1–N1–Ga1 94.4(6), C1–N2–Ga1 93.2(6), C35–N5–Ga3 93.0(6), C35–N6–Ga3 92.9(7), N4–C18–N3 105.0(7), C52–N7–Ga3 133.9(10).

1.943(4) Å). The bite angle accounts $68.1(2)^{\circ}$. The N₂CC-group is planar with an angle sum of 359.9° . The gallium atom is almost coplanar with the N₂CC-group (Ga(1)–N(1)C(1)N(2)C(2) 5.4(1) pm). The angle I(1)–Ga(1)–I(2) differs with 111.8(1)° slightly from the ideal 109.5° which is in the line with the Bent's rule.^{31,32}

3.4 Quantum chemical calculations

All DFT calculations have been performed with the *TURBO-MOLE* (*VERSION 6-1*) package using an RI approximation with a BP86 functional and def2-TZVP basis set.³³⁻⁴¹ The coordinates from the crystal structure analysis of **3**, **4** and **5** were used as starting points in geometry optimization and following Ahlrich-Heinzmann population analysis based on occupation numbers (SEN).⁴² The coordinates from the crystal structure analysis of **2** and **2a** were used for single point calculations in order to determine the dipole momentum.

The SEN for **3** (Table 2) show that there is a covalent bond with bond order one between the gallium atoms. The 2c-SEN for the N–C==N group lie in the typical range of delocalized double bonds, which agrees with the bond lengths being equal.

 Table 2
 2-centre Shared Electron Numbers in 3

Bond	2c-SEN	
Ga-Ga Ga-I Ga-N (terminal) Ga-N (centre) N-C==N	$\begin{array}{c} 1.32 \dots 1.33 \\ 0.91 \\ 0.82 \dots 0.84 \\ 0.82 \dots 0.83 \\ 1.62 \dots 1.63 \end{array}$	



Fig. 4 Crystal structure of 5. The thermal ellipsoids are given at the 25% probability level. Carbon bound hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–H1 1.54(6), Ga1–N1 2.009(7), Ga1–N2 2.021(6), Ga1–Ga2 2.457(2), Ga2–N4 2.013(6), Ga2–N3 2.029(6), Ga2–Ga3 2.463(2), Ga3–C52 1.988(9), Ga3–N6 2.006(7), Ga3–N5 2.026(6), N1–C1 1.346(9), N2–C1 1.339(9), N3–C18 1.34(1), N4–C18 1.346(9), N5–C35 1.337(9), N6–C35 1.344(8), C52–C53 1.53(2), Ga1–Ga3 4.288(2); H1–Ga1–N1 107(2), H1–Ga1–N2 112(2), N1–Ga1–N2 65.1(2), H1–Ga1–Ga2 121(2), N4–Ga2–N3 64.9(2), Ga1–Ga2–Ga3 121.3(1), C52–Ga3–N6 108.8(3), C52–Ga3–N5 107.4(3), N6–Ga3–N5 65.0(2), C1–N1–C6 134.7(7), C1–N1–Ga1 93.7(5), C1–N2–Ga1 93.4(4), C18–N3–Ga2 93.5(5), C18–N4–Ga2 94.1(5), C35–N5–Ga3 93.2(4), C35–N6–Ga3 93.9(5), N3–C18–N4 107.5(5), N5–C35–N6 107.8(6), C53–C52–Ga3 115.3(7).



Fig. 5 Crystal structure of 6. The thermal ellipsoids are given at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–I1 2.508(1), Ga1–I2 2.491(1), Ga1–N1 1.939(4), Ga1–N2 1.946(4), N1–C1 1.339(6), N1–C6 1.456(5), N2–C1 1.359(6), N2–C12 1.471(5), C1–C2 1.521(7); N1–Ga1–N2 68.1(2), I2–Ga1–I1 111.8(1), N1–C1–N2 107.4(4), N1–C1–C2 124.2(4), N2–C1–C2 128.3(4), N1–Ga1–I2 115.7(2), N2–Ga1–I2 117.4(2), N1–Ga1–I1 119.3(2), N2–Ga1–I1 118.4(2),C1–N1–Ga1 92.7(3), C1–N2–Ga1 91.8(3).

When looking at the charge distribution (Table 3) we see a positive cloud around the carbon atoms (except the methyl carbon atoms) and a negative cloud around the gallium atoms and iodine atoms. This results in a calculated dipole momentum of 5.2 Debye. For comparison only, the dipole momentum of thf (the most polar solvent we use) is about 1.8 Debye, according to calculations on the same level.

The dipole momentum of **3c** adds up to 8.3 Debye. So this could explain the uncommon dihedral angle in **3c**: the thf molecules create an electrostatic field which makes the trigallane to twist a little to become more polar.

 Table 3
 Atomic charges with multicentre corrections in 3

Atom	Charge
Ga (centre)	-0.06
Ga (terminal)	+0.04+0.05
I	-0.25
N (centre)	-0.08
N (terminal)	$-0.09 \dots -0.08$
N-C=N	+0.13+0.15
N-C(-C)=N	+0.03
$N_2CC(CH_3)_3$	$-0.04 \dots -0.03$
C_6H_{11} (ipso-C)	+0.10+0.12
C_6H_{11} (other-C)	$+0.01 \dots +0.03$
H	$-0.02 \dots +0.02$

 Table 4
 2-centre Shared Electron Numbers in 4

Bond	2c-SEN	
Ga–GaI	1.32	
Ga–GaNCMe ₂	1.33	
Ga–I	0.89	
Ga-N (centre)	$0.80 \dots 0.84$	
Ga–N (Ga–I)	0.810.83	
$Ga-N(Ga-(N_2C)-NCMe_2)$	0.730.82	
Ga-N (Ga-NCMe ₂)	1.16	
N-C=N	1.621.64	

Table 5 Atomic charges with multicentre corrections in 4

Atom	Charge	
Ga (centre)	-0.07	
Ga (Ga–I)	+0.03	
Ga (Ga-NCMe ₂)	+0.04	
I	-0.26	
N (centre)	-0.08	
N (Ga–I)	$-0.09 \dots -0.08$	
N (Ga- (N_2C) -NCMe)	-0.110.07	
N (Ga-NCMe ₂)	-0.14	
N-C=N	+0.13+0.15	
N-C(-C)=N	+0.03+0.04	
H	-0.02+0.03	

A similar effect occurs in the digallanes 2 and 2a. Since 2 has an inversion centre in the middle of the Ga-Ga bond, it has trivially no dipole momentum. 2a, cocrystallized with two thf molecules, is twisted (I-Ga-Ga-I dihedral 10.5°). This little change leads to a dipole momentum of 1.35 Debye.

The SEN (Table 4) and atomic charges (Table 5) of 4 are quite similar to the numbers in 3. The main skeleton is not affected by the substituent. The NCMe₂-group is bonded mainly covalently to the gallium.

The SEN (Table 6) and atomic charges (Table 7) in the gallium hydride 5 show the hydride and the ethyl group being charged slightly negative and bonded mainly covalently to the gallium.

In order to confirm our IR spectrum of 5, we calculated a vibrational spectrum, using the *aoforce*-module⁴³ of TURBOMOLE. The experimental absorption of 1755 cm⁻¹ could be reproduced quite well with a calculated wave number of 1760 cm⁻¹.

Conclusion 4

Using dicyclohexylneopentylamidinate residues has shown to be an excellent pathway to trigallanes. The Ga₃-unit formed by

Table 6 2-centre Shared Electron Numbers in 5

Bond	2c-SEN	
HGa–Ga	1.35	
EtGa–Ga	1.37	
EtGa–N	0.770.79	
Ga-N (remaining)	0.790.85	
N-C=N	1.621.63	
Ga–H	1.28	
Ga–C	1.27	

 Table 7
 Atomic charges with multicentre corrections in 5

Atom	Charge
Ga (centre)	-0.10
Ga (HGa)	-0.06
Ga (EtGa)	+0.05
N	$-0.09 \dots -0.06$
C (GaEt)	-0.13
N-C=N	+0.12+0.13
N-C(-C)=N	+0.04
H (gallium bound)	-0.10
H (carbon bound)	-0.02+0.03

a disproportionation of Ga(I) to Ga(II) and Ga(0) is stable in metathesis reactions. This is the first example of amidinate stabilised gallium(I) compounds. Using sodium superhydride it has been possible to obtain the first example of a gallium(II) hydride. The oxidation state of the trigallane has been confirmed by redox-titration. These functional di- and trigallanes offer a wide perspective for preparing rings and cages with oligogallium cores.

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