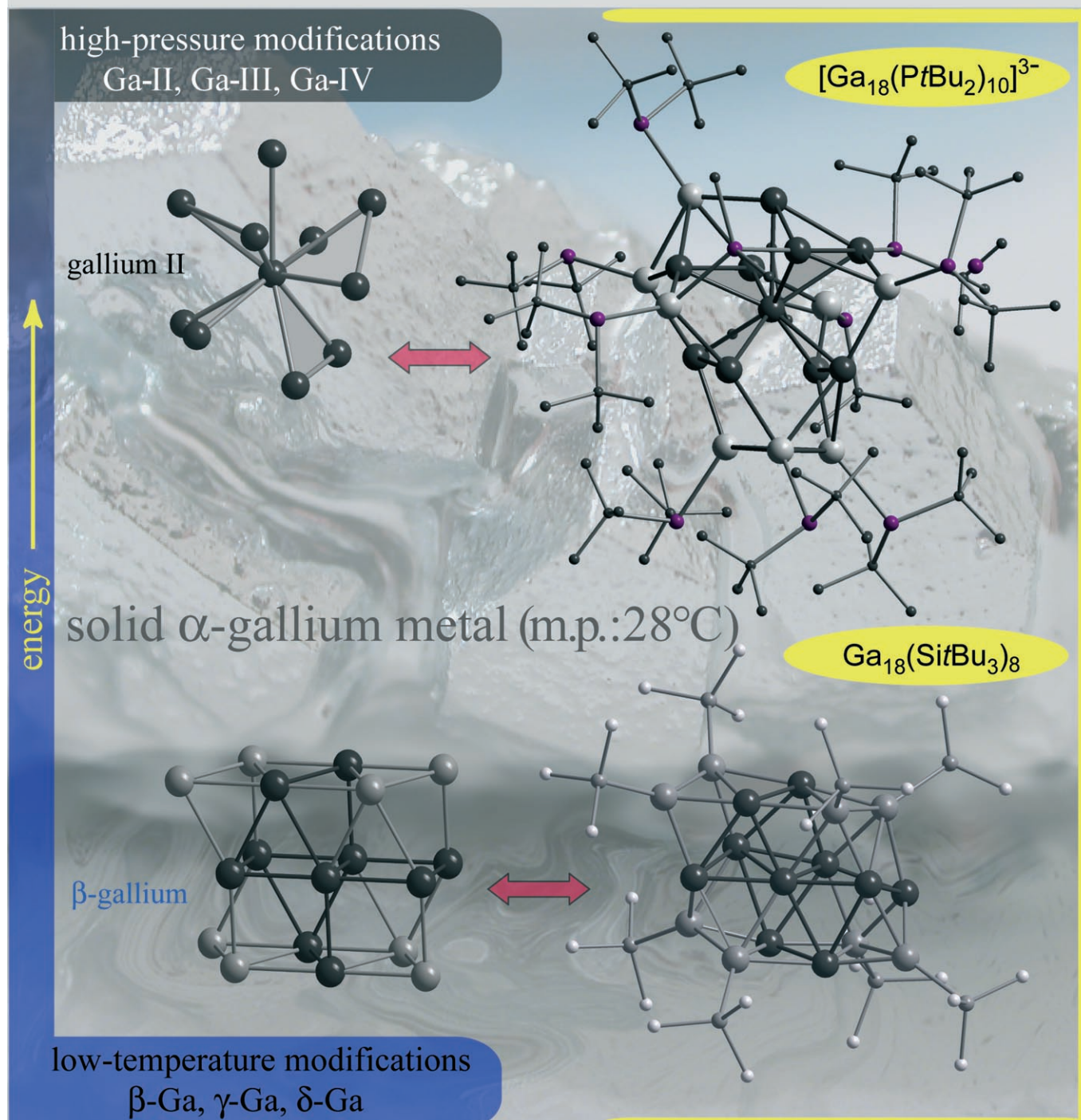Two metalloid Ga_{18} clusters

and their topological and energetic relation to the

element modifications β-Ga and Ga-II

For more information see the following pages

high-pressure modifications
Ga-II, Ga-III, Ga-IV

$[Ga_{18}(PtBu_2)_{10}]^{3-}$

gallium II

solid α-gallium metal (m.p.:28°C)

$Ga_{18}(SitBu_3)_8$

β-gallium

low-temperature modifications
β-Ga, γ-Ga, δ-Ga

VIP A Second Metalloid Ga$_{18}$ Cluster and Its Topological Similarity to the High-Pressure Ga-II Modification

Jochen Steiner and Hansgeorg Schnöckel*[a]

Abstract: The topology of many modifications of elemental gallium is reflected in the large variety of metalloid Ga clusters that have been isolated as intermediates on the way from the metastable molecular GaX species (X = Cl, Br, I) by means of disproportionation to the bulk metal. Herein, we report the synthesis and characterization of the first metalloid cluster anion [Ga$_{18}$-(PtBu$_2$)$_{10}$]$^{3-}$ with the singular core topology that resembles the gallium high-pressure modification Ga-II. The stabilization of the cluster anion through ion-pair contacts with a chainlike "Li$_4$Br$_2$ backbone" is discussed. Furthermore, the compound is discussed in context of the other metalloid clusters Ga$_{18}$R$_8$ and Ga$_{22}$R$_8$ (R = SitBu$_3$) and their structural relation to the elemental modifications Ga-III and β-Ga, respectively.

Keywords: cluster compounds · gallium · metal–metal interactions · structure elucidation

Introduction

We recently reported the synthesis of metalloid[1] gallium cluster compounds[2,3] in which the sterically demanding phosphanide ligands PR$_2$ (R = tBu$_2$) lead to structures that are analogous to modifications of elemental gallium. For example, the central coordination polyhedra in the neutral cluster compound [Ga$_{22}$R$_{12}$] (**1**)[2] are Ga$_{12}$ icosahedra (δ-gallium) and centered Ga$_{13}$ cubeoctahedra (face-centered cubic Ga-IV) in the anionic cluster [Ga$_{51}$R$_{14}$Br$_6$]$^{3-}$ (**2**).[3] By comparing the volume of the central Ga$_{12}$ or Ga$_{13}$ polyhedra in the cluster compounds **1** and **2**, respectively, with the corresponding gallium modification it has been shown by quantum chemical single-point calculations that the cluster cores of **1** and **2** are "compressed"; this compression can be explained to some extent by the constricting effects of the PtBu$_2$ ligands (cf. below). In addition to the lower-volume elementlike central core units in **1** and **2**, a "compressed" Ga$_4$ core is also observed in the neutral cluster compound [Ga$_{16}$(PtBu$_2$)$_{10}$] (**3**).[4] What is the basis for this "compression"?: In contrast to the previously used ligands,[5] for example, -N(SiMe$_3$)$_2$ or -C(SiMe$_3$)$_3$, the PtBu$_2$ ligand is characterized by its ability to form bridging coordination modes in addition to occupying terminal positions on the cluster framework.[2,3] The number of phosphanide ligands in terminal and bridging positions is similar in the reported compounds **1** (6:6), **2** (6:8), and **3** (6:4).

In this publication we report the synthesis of the novel cluster compound [Ga$_{18}$(PtBu$_2$)$_{10}$][Li$_5$Br$_2$(thf)$_9$] (**4**) and the bonding within its [Ga$_{18}$(PtBu$_2$)$_{10}$]$^{3-}$ cluster ion (**4a**), which differs significantly from the cluster species **1**–**3** in terms of the coordination modes of the PtBu$_2$ ligand. Additionally, cluster anion **4a** can be compared to the recently synthesized metalloid cluster compound [Ga$_{18}$(SitBu$_2$)$_8$] (**5**),[6] in which the bulkier SitBu$_3$ ligands (supersilyl) shield the cluster core in terminal positions and cannot take part in bridging coordination. The ladderlike arrangement of the central Ga$_{10}$ framework in **5** exhibits a high resemblance to the structure of β-Ga.[6,7] The topology of the gallium atoms in the herein reported Ga$_{18}$ cluster (**4a**) can therefore be seen as another piece of the puzzle in completing the understanding of the formation of intermediates on the way to one of the seven modifications of the gallium metal bulk phase.[8]

Results and Discussion

To synthesize different metalloid gallium cluster compounds with PtBu$_2$ ligands, solutions of the metastable, subvalent GaX (X = Cl, Br) have to be partially disproportionated in absence of the ligand by a controlled temperature increase.[5,8] This procedure leads to the formation of gallium-rich [Ga$_n$X$_m$] clusters ($n \geqslant m$) prior to the addition of the

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phosphanide ligand, which suppresses subsequent growth of the cluster after the substitution of the halide function. The number of aggregated gallium atoms in the formed metalloid clusters is therefore directly linked to the temperature at which the metathesis of solutions of the LiPtBu$_2$ ligand and Ga^I halide is carried out. The general relationship between cluster size and reaction temperature could be verified and extended to other ligands with the synthesis of different metalloid gallium and aluminium clusters; the largest clusters were obtained when solutions of the metastable Ga^{I}X/Al^{I}X species were gently heated until formation of the metal by disproportionation just began.[6, 8]

In our experiment, a metastable solution of GaBr in toluene/THF[5] in a ratio of 3:1 was added to the solid LiPtBu$_2$ ligand at −78 °C. The reaction suspension was slowly warmed to −45 °C and then diluted with toluene in order to get a homogenous solution and to initiate the substitution process. After stirring the reaction mixture at room temperature for 24 h, the solution is warmed to +60 °C for a further 24 h.

Compound **4** crystallizes at ambient temperature and under slightly reduced pressure within one week in form of black rhombohedrons. The most striking feature of the crystal structure[9] is the formation of two ion-pair contacts between the cluster anion [Ga$_{18}$(PtBu$_2$)$_{10}$]$^{3-}$ (**4a**) and a [Li-(thf)]$^+$ cation (Li1, Figures 1 and 2) as well as a [Li$_4$Br$_2$-(thf)$_8$]$^{2+}$ cation (connected by Li3, Figures 1 and 2). These anion–cation interactions are, as far as we know, the first re-
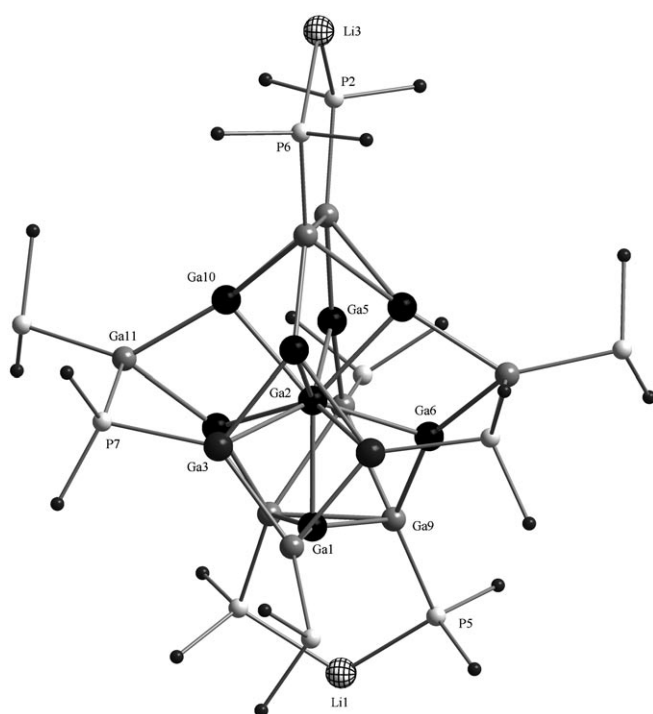

Figure 1. Representation of the cluster **4a** in **4** including the two phosphanide coordinated Li ions. The Ga atoms of the cluster core that resemble the Ga-II modification are highlighted in black. Selected bond lengths in Å: Ga2−Ga1 2.62(2); Ga2−Ga3 2.74(7), Ga2−Ga5 2.55(4), Ga2−Ga6 2.66(5), Ga2−Ga10 2.66(8), Li1−P5 2.48(8), Li3−P2 2.61(3), Li3−P6 2.69(0).
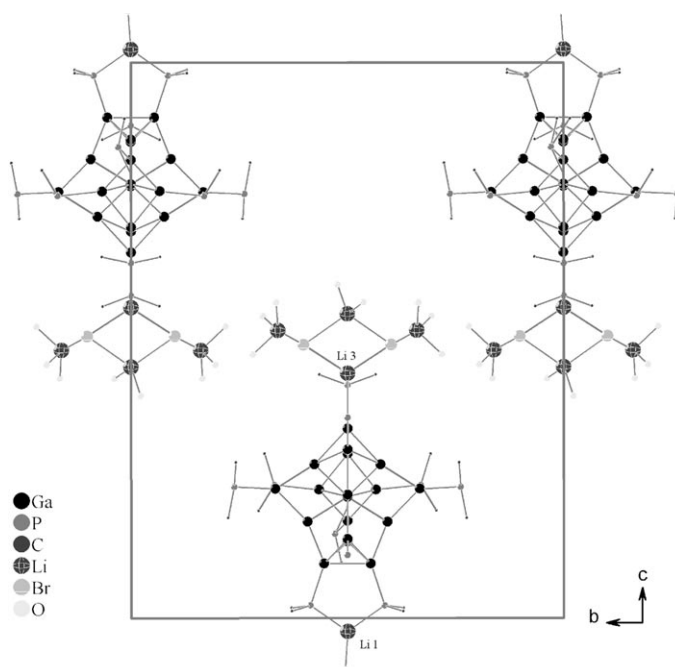

Figure 2. View of the elemental cell ($b = 23.35$ Å and $c = 30.76$ Å) along the crystallographic a axis of **4** with central Li$_4$Br$_2$ backbone. For clarity, only the bonds from phosphorus to the αC atoms in the PtBu$_2$ ligands and the O atoms of the Li coordinating THF molecules are shown. All hydrogen atoms are omitted.

ported in the field of metal-rich cluster compounds. The formation of these interactions is plausible due to the crystallization conditions, in which the reduced pressure prevents complete solvation of the cations by THF molecules present in the solvent mixture. The coordination of the phosphorus lone pair to the lithium cation substitutes the missing THF molecules and leads to a stabilization by forming the energetically favored ion–pair contacts.

The single-crystal x-ray structural analysis of **4** reveals a chainlike arrangement of the cluster anions in the crystal, in which an alternating orientation of the anions along a partly solvated "Li$_4$Br$_2$" backbone[10] is realized (Figure 2). This chainlike structure can be seen as the result of optimized electrostatic interactions and the steric demand of the bulky [Ga$_{18}$R$_{10}$]$^{3-}$ (**4a**) ions.

Significantly, the cluster anion **4a** has eight of its ten ligands occupying terminal positions and just two taking part in bridging coordination (Figure 1), in contrast to the phosphanide-stabilized cluster compounds **1**, **2**, and **3**. The two *trans*-orientated ion contacts are realized by two terminal coordinated phosphanide ligands through their lone pairs. The threefold negative charge of the cluster anion **4a** is derived from this arrangement, which also leads to an odd number of electrons due to an even number of gallium and phosphorus atoms. The radical character of **4** is supported by solid-state EPR measurements[11] that reveal a g factor of 2.0028, a value close to the one of a free electron and therefore an example of a well-separated spin system.

The core of the "body-centered" cluster anion **4a** has lower symmetry in contrast to the polyhedral central Ga$_n$

units in the compounds **1** (icosahedron), **2** (cube-octahedron), and **3** (tetrahedron). The structure of **4a** can best be described in allusion to the coordination sphere of the gallium atoms in the recently re-determined high-pressure modification Ga-II.[5,12] In this gallium modification, which can be understood as a layered structure in analogy to the modifications of Cs-III[13] or the high-pressure modification of lithium,[14] the gallium atoms have an average coordination number of ten (mainly 8+2). The coordination sphere of the 14(!) crystallographic independent Ga atoms in the Ga-II phase can be distinguished by their Ga−Ga bond lengths in two different subspheres with distances of 2.65–3.1 Å and 3.1–3.3 Å (Figure 3, right), whereas on average eight of the ten surrounding gallium atoms are in the coordination sphere from 2.65–3.1 Å and two are between 3.1–3.3 Å. The coordination number of nine in **4a** is just between that of
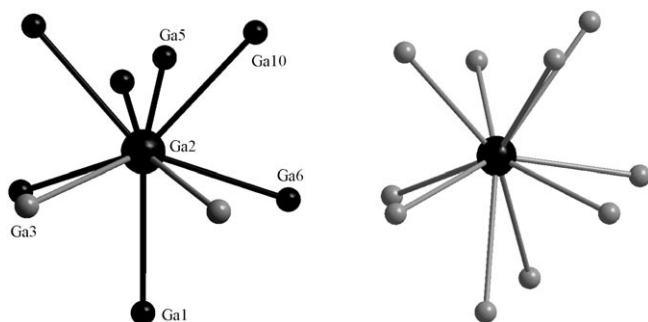

Figure 3. Comparison of the gallium coordination sphere in **4a** (left) and the high-pressure modification Ga-II (right). The gallium atoms are labeled as in Figure 1.

the 14 different Ga atoms of Ga-II with eight shorter and two longer Ga−Ga distances. As expected, the Ga−Ga bond lengths in **4a** as a molecular species are shorter than observed in Ga-II; they are in the range 2.55–2.77 Å with an average value of 2.67 Å. [Note: This relation of shorter bonds in molecular clusters in comparison to the bulk metal phase has been shown many times:[5] The larger bonds in the bulk metal are mainly caused by the high coordination numbers of all metal atoms, while in a cluster the central metal atom has a higher coordination number than the outer ones.] Thus, the coordination number of nine (Figure 3, left) and the topology of this coordination sphere show for the first time a strong analogy of a metalloid cluster compound to the high-pressure phase Ga-II (Figure 3, right).

The bond lengths in the cluster core of **4a** (cf. Figure 1) are in the range of the distances observed in formerly characterized metalloid gallium cluster compounds (2.68–2.77 Å in **3**, 2.58–2.8 Å in **1**), but significantly shorter than in **2** with 2.79–2.95 Å (due to the high coordination number of twelve). The gallium–gallium bonds from the atoms of the first coordination sphere to the outer gallium atoms in **4a** are shorter, with an average value of 2.56 Å, and reflect the increasing covalent character of these bonds and the higher oxidation state of the involved atoms: that is, the outer,

ligand bearing gallium atoms of the GaPR$_2$ moieties have an oxidation state of +I.

Not only the unusual coordination sphere of the central gallium atom in **4a**, but especially the relatively high number of terminally bonded ligands, makes this compound so unique among all other gallium phosphanide clusters. Eight out of ten phosphanide ligands are connected to the cluster framework in a terminal fashion with bond lengths between 2.37 and 2.39 Å, that is, only slightly longer than in crystalline GaP (2.35 Å). The two bridging phosphanide ligands form nearly symmetric gallium–phosphorus bonds of 2.43 and 2.45 Å with an inner angle of 96.4° (P7, Figure 1), which is similar to some of the bridging Ga−P bonds in compounds **1**, **2**, and **3** but different from the situation in normal valent R$_2$GaP$_2$GaR$_2$ species. Thus, similar bonds within Ga-P-Ga bridges like in **4a** and some other metalloid Ga clusters (**1**, **2**, and **3**) indicate a more delocalized bonding situation (four-electron three-center bonds), while normal "asymmetric" Ga-P-Ga bridges (c.f. also above) are characteristic for donor–acceptor behavior without significant electron delocalization.[17]

In comparison to the other gallium cluster compounds with shielding phosphanide ligands (**1**, **2**, and **3**), the question arises whether the high negative charge (−3) on the clusters suppresses further bridging modes of the ligands (with their lone pairs) or whether the low number of bridging ligands makes an external reduction necessary to stabilize the cluster framework. In any case, the formation of the two ion contacts by four terminal ligands and the two Li cations contribute significantly to the stabilization and the observed structure of cluster **4a** (Figure 2). Furthermore, the direct ion contacts between the cluster anion **4a** and the Li cations also prohibit further bridging arrangements of the phosphanide ligands within the cluster framework. The experimental proof for this kind of stabilization derives from attempts to dissolve the compound **4** in THF, as we observed the dissociation of the phosphorus lithium contacts and the complete solvation of the Li cations. This solvation of the stabilizing contact pairs results in a rearrangement or degradation of the cluster, which was indicated by ^{31}P NMR measurements.[15]

Conclusion

Cluster **4a** is of fundamental importance for the so far unique structural systematics of metalloid gallium cluster compounds: the many examples reported by our group lead to the conclusion that these Ga cluster compounds can be understood as intermediates on the way to the gallium metal. In particular, the parameters for the synthesis of these metalloid clusters are instrumental in determining the reaction pathway that results in one of the seven different modifications of elemental gallium. Because this connection was recently reported in a review article,[8] we will only discuss the structural relationship of **4a** to the high-pressure modification Ga-II. This relationship is particularly interest-

ing in comparison to the Ga_{18} cluster (**5**) that exhibits a structural analogy to the β-gallium, a phase stable under ambient conditions (Figure 4, bottom). We therefore conclude that the P*t*Bu$_2$ ligands in **4a** are less bulky than the Si*t*Bu$_3$ ligands in **5**, and can therefore also act as bridging agents. This results in a denser, body-centered framework for **4a**
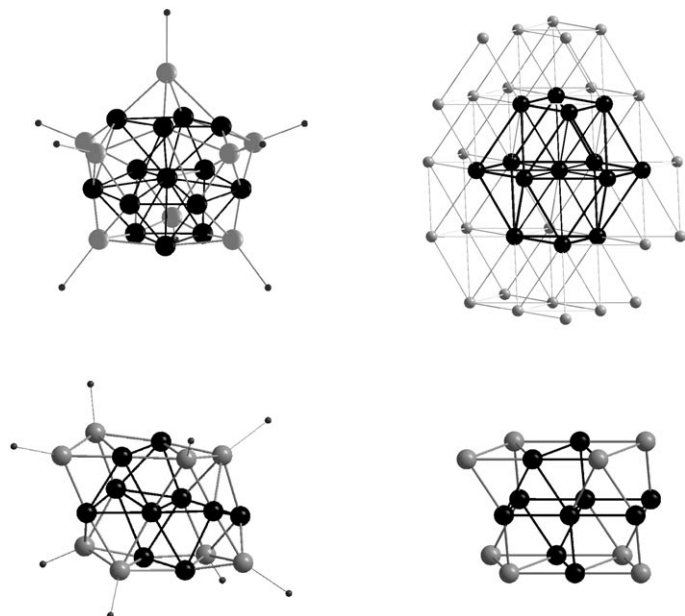

Figure 4. Representation of the metalloid gallium cluster compounds $[Ga_{22}(SitBu_3)_8]$ (**6**, top left) and $[Ga_{18}(SitBu_3)_8]$ (**5**, bottom left) and the section of their corresponding elemental modifications Ga-III (top right) and β-gallium (bottom right).

(while the number of 18 gallium atoms is the same for **4a** and **5**!). In terms of density, the "body-centered" Ga_{18} cluster **4a** (with analogy to the high-pressure phase Ga-II) lies between that of the cluster $[Ga_{18}(SitBu_3)_8]$ (**5**) and that of the "centered" cluster $[Ga_{22}(SitBu_3)_8]$ (**6**)[6] (Figure 4, top). The latter, with its very similar ligand shell of six Si*t*Bu$_3$ substituents, has a coordination number of 13 for the central Ga atom, and the architecture of the inner Ga_{14} unit strongly resembles that of the high-pressure modification Ga-III.[6,16] The increasing density of the central Ga_n units (Ga_{10}, Ga_{10}, and Ga_{13}) from the three clusters **5**, **4a**, to **6** thus represents the topologies of the three gallium modifications β-Ga, Ga-II, and Ga-III that are realized under increasing pressure.

Experimental Section

A solution of Ga^{I}Br (3.2 mmol) in toluene/THF (3:1 10 mL)[5] was added to LiP*t*Bu$_2$ (610 mg, 4.0 mmol) at −78 °C. The reaction mixture was warmed to −45 °C within 3 h and then diluted with toluene (30 mL), causing the reaction temperature to rise to −20 °C. After 4 h, the solution reached room temperature and was stirred for further 24 h, resulting in a dark black solution without any precipitate. This solution was then warmed to +60 °C under reduced pressure (ca. 500 mbar) for 24 h, and

afterwards the compound **4** crystallizes at room temperature within one week. Yield 25 mg, that is, this amount could be separated from the reaction mixture.

[1] A. Schnepf, G. Stößer, H. Schnöckel, *J. Am. Chem. Soc.* **2000**, *122*, 9178.

[2] J. Steiner, G. Stößer, H. Schnöckel, *Angew. Chem.* **2004**, *116*, 6712; *Angew. Chem. Int. Ed.* **2004**, *43*, 6549.

[3] J. Steiner, G. Stößer, H. Schnöckel, *Angew. Chem.* **2004**, *116*, 306; *Angew. Chem. Int. Ed.* **2004**, *43*, 302.

[4] J. Steiner, G. Stößer, H. Schnöckel, *Angew. Chem.* **2003**, *115*, 2016; *Angew. Chem. Int. Ed.* **2003**, *42*, 1971.

[5] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532.

[6] A. Donchev, A. Schnepf, G. Stößer, E. Baum, H. Schnöckel, T. Blank, N. Wiberg, *Chem. Eur. J.* **2001**, *7*, 3348.

[7] L. Bosio, A. Defrain, *Acta Crystallogr. Sect. B* **1969**, *25*, 995.

[8] H. Schnöckel, *Dalton Trans.* **2005**, *19*, 3131.

[9] Crystal parameters of $[Ga_{18}(PtBu_2)_{10}][Li_5Br_2(thf)_9]$ (**4**): $M_r = 3547.26$; crystal dimensions $0.2 \times 0.2 \times 0.05$ mm, monoclinic, space group $C2/m$, $a = 22.684(5)$, $b = 23.3488(5)$, $c = 30.755(6)$ Å, $\beta = 101.69(3)°$, $V = 15\,951$ Å^3, $Z = 4$, $\rho_{calcd} = 1.689$ g cm^{-3}, $\mu_{Mo} = 3.643$ mm^{-1}, $\theta_{max} = 22.5°$, 62735 observed reflections, 12859 independent reflections ($R_{int} = 0.156$), absorption correction: numerical (min/max transmission 0.6679/0.8904), $R1 = 0.0581$, $wR2 = 0.1417$. Stoe IPDS-Diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 150 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXTL (G. M. Sheldrick, University of Göttingen). CCDC-294803 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] A comparable structural motif to the partly solvated, saltlike Li_4Br_2 fragment can also be found in the cationic counterpart $[Li_4Cl_2$-$(Et_2O)_{10}]$ of the anionic organocopper–lithium cluster compound $[Li_2Cu_3Ph_6]$. H. Hope, D. Oram, P. P. Power, *J. Am. Chem. Soc.* **1984**, *106*, 1149.

[11] Measured by Dr. B. Pilawa, Physical Institute, University of Karlsruhe.

[12] O. Degtyareva, M. I. McMahon, D. R. Allan, R. J. Nelmes, *Phys. Rev. Lett.* **2004**, *93*, 205502.

[13] M. I. McMahon, R. J. Nelmes, S. Rekhi, *Phys. Rev. Lett.* **2001**, *87*, 255502.

[14] M. Hanfland, K. Syassen, N. E. Christensen, D. L. Novikov, *Nature* **2000**, *408*, 174.

[15] Due to the radical character of compound **4** we would not expect to get a ^{31}P NMR spectrum without manual optimization of the magnetic field. However, we could obtain a routine spectrum with a number of sharp ^{31}P resonances (more than expected for **4a**), indicating that the measured solution contains new, nonradical species. It also shows, that the cluster framework is not completely destroyed, because: 1) no elemental gallium is observed, 2) no signal for Ga(P*t*Bu$_2$)$_3$ is detected, and 3) the color of the solution remains dark black (as before the addition of THF), which indicates that larger clusters with Ga−Ga bonds are still present.

[16] L. Bosio, *J. Chem. Phys.* **1978**, *68*, 1221.

[17] J. Steiner, Ph.D. Thesis, University of Karlsruhe (Germany), **2004**.