DOI: 10.1002/anie.200905920

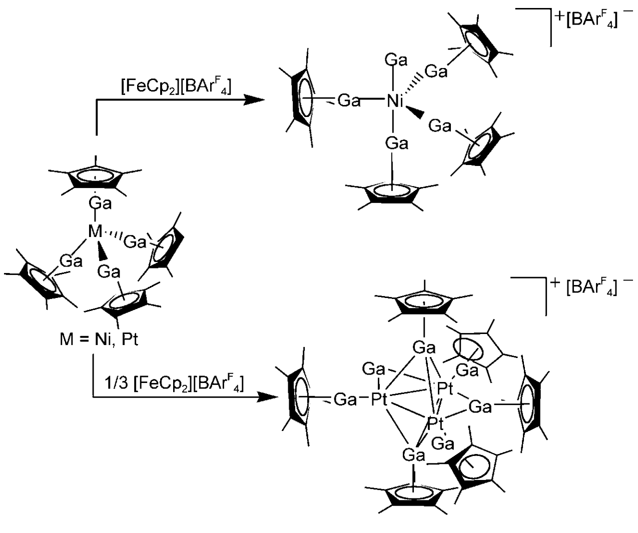
Selective Oxidative Cleavage of Cp* from Coordinated GaCp*: Naked Ga^+ in $[GaNi(GaCp^*)_4]^+$ and $[(\mu_2\text{-}Ga)_nM_3(GaCp^*)_6]^{n+}$ **

*Markus Halbherr, Timo Bollermann, Christian Gemel, and Roland A. Fischer**

The coordination chemistry of monovalent compounds comprising a Group 13 element E and an organic group R at a metal center M[1] offers a unique molecular access to novel compounds linking metal-rich complexes and clusters with the solid-state chemistry of metal alloys. In particular, the soft chemical synthesis of M–E Hume–Rothery phases (NiAl, NiGa, PtGa, CuAl, CuGa, etc.) as colloidal nanoparticles or as powders were achieved by using combinations $[L_nM]$ (L = hydrocarbon) and ER of precursors or by employing tailored single-source precursors with direct M–E bonds.[2] Similarly, α-,β-,γ-Cu/Zn colloids, "nano-brass", were obtained from [CpCuL] with $ZnCp^*_2$ as precursors ($Cp = C_5H_5$, $Cp^* = C_5Me_5$).[3] Furthermore, $Cp^*\text{–}CH_3$ and Zn–Ga exchange reactions allow the formation of the unusual compounds $[Mo(ZnMe)_9(ZnCp^*)_3]$ and $[(CO)_{16}Mo_4Zn_6(ZnCp^*)_4]$ from $[(CO)_{6-n}Mo(GaCp^*)_n]$ ($n = 0$, 2) and $ZnMe_2$. Both Mo–Zn compounds represent molecular cut-outs of the solid-state structure of Mo–Zn intermetallics.[4]

The cleavage of the "protecting" Cp* group from transition-metal bound ECp* ligands is a pertinent aspect of this novel chemistry. For example, the selective protolysis of $[Pt(GaCp^*)_4]$ by $[H(OEt_2)_2](BAr^F{}_4)$ yields $[GaPt(GaCp^*)_4](BAr^F{}_4)$ and $[Pt_2H(Ga)(GaCp^*)_7](BAr^F{}_4)_2$ ($BAr^F{}_4 = B[3,5\text{-}(CF_3)_2C_6H_3]_4$).[5] Also, the hydrogenation of [Ru(cod)(cot)] (cod = 1,4-cyclooctadiene, cot = 1,3,5-cyclooctatriene) in the presence of GaCp* gives the highly fluxional diruthenium complex $[Ru_2(Ga)(GaCp^*)_7(H)_3]$, featuring a linear Ru–Ga–Ru unit.[6] Herein we now report a new and selective method for a facile cleavage of Ga–Cp* bonds. The treatment of $[M(GaCp^*)]_4$ (M = Ni, Pd, Pt)[7] with $[Fe(C_5H_5)_2](BAr^F{}_4)$ leads to a surprisingly selective oxidative cleavage of the Cp* group leaving the oxidation state of Ga^I and M unchanged and yields the products shown in Scheme 1, Figure 1, and Figure 2.

The cation $[GaNi(GaCp^*)_4]^+$ (**1**)[8] was obtained as its BAr_4 salt by treatment of $[Ni(GaCp^*)_4]$ with an equimolar amount of $[Fe(C_5H_5)_2](BAr^F{}_4)$ in fluorobenzene at 25 °C in reproducible yields (80 %), and characterised by ^1H NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The ^1H NMR spectrum shows two broad signals arising from the cation **1** indicating fluxional GaCp* ligands. In situ NMR experiment of the reaction mixture reveals one characteristic signal for decamethylfulvalene (Cp^*_2), while the other signals for this by-product are masked by broad peaks from GaCp*. No other side products were detected that would indicate either the oxidation of Ga^I or of the transition-metal center. Also no Ga-F species were formed. This unexpected selectivity of the reaction for oxidative cleavage of the Cp* is quite surprising.



Scheme 1. Reaction of $[M(GaCp^*)_4]$ (M = Ni, Pt) with $[Fe(C_5H_5)_2](BAr^F{}_4)$.

Compound $\mathbf{1}BAr^F{}_4$ crystallizes in the monoclinic space group *P21/c*. The cation **1** exhibits a slightly distorted trigonal-bipyramidal structure with the Ga^+ ligand in an axial position (Supporting Information, Figure S1), as in the homologous $[GaPt(GaCp^*)_4]^+$.[5] The equatorial GaCp* ligands are bent towards the terminal Ga^+ ligand (Ga1) and the Ga1-Ni-Ga(n) angles ($n = 3$, 4, 5) are closer to 80° than 90°. The equatorial Ni–Ga bond lengths average to 2.246 Å and are thus slightly longer than those of the parent complex $[Ni(GaCp^*)_4]$ (average = 2.219 Å). Interestingly, the Ga1–Ni bond length (2.361(1) Å) is close to the value for the axial Cp*Ga–Ni bond (2.320(1) Å), both bonds being slightly elongated with respect to the equatorial ones. The bonding situation of substituent-free ("naked"), terminally coordinated Ga^+ was elucidated in detail and can be described as a main-group-metal equivalent of the proton H^+.[5] Note that Ga^+ exhibits

---

[*] M. Halbherr, T. Bollermann, Dr. C. Gemel, Prof. Dr. R. A. Fischer
Inorganic Chemistry II – Organometallics & Materials, Ruhr Universität Bochum
Universitätsstrasse 150, 44870 Bochum (Germany)
Fax: (+49) 234-321-4174
E-mail: roland.fischer@rub.de
Homepage: http://www.ruhr-uni-bochum.de/aci2/

[**] . This work was funded by the project "Metal-Rich Molecules" of the German Research Foundation (DFG, Fi-502/24-1). The authors thank Prof. Dr. Ramaswamy Murugavel, IIT Bombay, for valuable discussions. Transition-metal complexes of Group 13 metals, Part 67. (M = Pd, $n = 2$; M = Pt, $n = 1$).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905920.

both, strong σ- and as well π-acceptor capacity but no donor properties at all. Complex **1** is only the third example of this unusual kind of terminal coordinated Ga^I species. In addition to the above-mentioned Pt congener of **1**, the complex $[GaRu(PCy_3)_2(GaCp^*)_2]^+$ has been reported.[9] Note that there are no short contacts between the F atoms of the $BAr^F{}_4{}^-$ ion and the naked Ga atoms in **1** or in the related compounds.[5,6,9]

Interestingly, treatment of the platinum complex $[Pt(GaCp^*)_4]$ with $[Fe(C_5H_5)_2](BAr^F{}_4)$ under the same conditions used for the synthesis of **1** did not yield the homologous cation $[GaPt(GaCp^*)_4]^+$. Instead the formation of the trimeric cluster cation $[(\mu_2\text{-}Ga)Pt_3(GaCp^*)_6]^+$ (**2**)[11] was strongly favored, regardless of the molar ratio of the reaction partners. Compound **2**$BAr^F{}_4$ crystallizes in the monoclinic space group *Pm* with one molecule in the unit cell. The molecular structure (Figure 1) consists of a central triangular Pt_3 unit which is capped by two μ_3-GaCp* ligands, which are symmetrically equivalent, resulting in a trigonal bipyramid. Each Pt atom bears one additional terminal GaCp* ligand, while only two of the three Pt–Pt edges are bridged by gallium ligands, that is, one by GaCp* and the other one by Ga^+. Interestingly, the Pt−Pt distances are rather different from each other. The μ_2-GaCp* bridge leads to the shortest bond of 2.594(2) Å. The μ_2-Ga^+ bridged Pt−Pt bond is 2.691(2) Å and the remaining ligand-free edge of the Pt_3 triangle has the longest bond of 2.802(2) Å. The μ_2-Ga^+ ligand bridges asymmetrically with Pt−Ga bonds of 2.596(4) and 2.379(3) Å, values which compare with the terminal Pt−Ga^+ bond in $[GaPt(GaCp^*)_4]^+$ of 2.459(1) Å. The average value of the Pt−Ga bond lengths of the terminal ligands is 2.310 Å. The respective Pt−Ga distances for the two μ^3-GaCp* ligands of 2.540 Å are slightly shorter than for the μ^2-GaCp* (2.593 Å). As for **1**, all the Cp* groups are bound in an almost ideally symmetric η^5-mode with average contacts $Cp^*_{centroid}$−Ga of 1.902 Å for the terminal GaCp*, 2.027 Å for the μ_2-GaCp*, and 1.948 Å for the μ_3-GaCp* ligands. These data are fully consistent with the typical bonding parameters of GaCp* ligands in homoleptic complexes $[M_a(GaCp^*)_b]$ with M in the oxidation state zero.[1e]

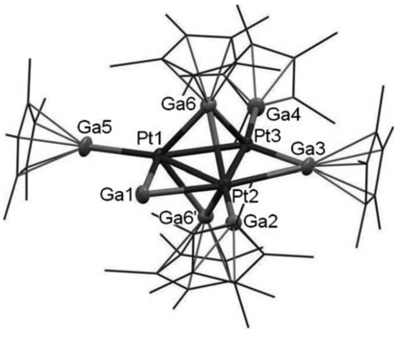


Figure 1. Molecular structure of the cation **2** (Hydrogen atoms and anion are omitted for clarity). The substituent-free Ga^+ ligand is denoted as Ga1. Selected bond lengths [Å] and angles [°]: $Cp^*_{centroid}$–Ga2 1.896, $Cp^*_{centroid}$–Ga3 2.017, $Cp^*_{centroid}$–Ga4 1.928, $Cp^*_{centroid}$–Ga5 1.963, $Cp^*_{centroid}$–Ga6 1.945. Ga1–Pt1 2.379(3), Ga1–Pt2 2.598(4), Pt1–Pt2 2.693(2), Pt2–Pt3 2.597(2), Pt1–Pt3 2.803(2), Pt2–Ga2 2.282(3), Pt2–Ga3 2.856(4), Pt3–Ga3 2.332(3), Pt3–Ga4 2.292(3), Pt1–Ga5 2.346(3), Pt1–Ga6 2.532(3), Pt2–Ga6 2.562(3), Pt3–Ga6 2.525(3); Pt1-Ga1-Pt2 65.33(9), Pt2-Ga3-Pt3 59.06(8).

Since there is no other Pt–Ga clusters containing three Pt atoms reported yet, cation **2** can be compared with the only known reference compound of similar composition and structure, namely $[Pd_3(AlCp^*)_6]$.[10] The occurrence of two face-bridging ECp* groups in both structures, in addition to terminal and edge-bridging groups, is likely to be related to the steric bulk of the Cp* ligand. From polyhedral skeletal electron pair theory (PSEPT) and Wade–Mingos electron-counting rules a triangular $[M_3L_a]$ unit may be stable with 48 or fewer valence electrons.[12] Triangular Pt_3 clusters are typically electron deficient, $[Pt_3(CO)_6]^{2-}$ has only 44 valence electrons.[13] The electron count of the neutral $[Pd_3(AlCp^*)_6]$ is only 42. As in **1**, the edge bridging Ga^+ in **2** acts as pure Lewis acid without any substantial donation which results in an electron count of 42. It is interesting to note that a typical reaction involving transition-metal carbonyl clusters is also protonation. For example, $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ (also a triangular 42 electron cluster) can be protonated by HBF_4 in diethyl ether to yield $[(\mu_3\text{-}H)Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3](BF_4)$.[14] The preference of edge-bridging over the face bridging for Ga^+ in **2** is certainly caused by steric effects of the other GaCp* groups. The ^{1}H NMR spectrum of **2**$BAr^F{}_4$ in C_6H_5F/10% C_6D_6 at room temperature exhibits three signals at $\delta = 2.08$, 1.99, and 1.46 ppm with a 1:1:1 ratio assigned to the terminal, the doubly bridging, and the triply bridging GaCp* ligands, respectively. The structure in solution is clearly different to the solid-state structure (see Figure 1) which contains one μ_2-GaCp*, two μ_3-GaCp*, and three terminal GaCp* ligands. However, the high-temperature ^{1}H NMR spectrum (60 °C) shows broadening of the signals for the μ_3-GaCp* and μ_2-GaCp* ligands, indicating an intramolecular process exchanging these ligand positions.

Cation **2** also is accessible by two other synthetic routes. **2**$BAr^F{}_4$ can be obtained in 80% yield by treatment of $[Pt(GaCp^*)_4]$ with 0.33 molar equivalents of $[H(OEt_2)_2](BAr^F{}_4)$ in fluorobenzene at room temperature with Cp*H being produced as the by-product in stoichiometric amounts. The third synthetic route to yield **2** involves a more complex redox reaction between $[(cod)Pt(CF_3SO_3)_2]$ and excess GaCp* in fluorobenzene. The reduction of Pt^{II} to Pt^0 is accompanied by the corresponding oxidation of GaCp* to form the unusual counter anion $[Cp^*{}_2Ga(CF_3SO_3)_2]^-$ which removes one Cp* ligand from a Ga^I (see the Supporting Information).

Although the reaction of the palladium complex $[Pd(GaCp^*)_4]$ with $[Fe(C_5H_5)_2](BAr^F{}_4)$ leads to a mixture of several complexes which could not be separated and analyzed, the treatment of the trimeric complex $[Pd_3(GaCp^*)_8]$ with $[Fe(C_5H_5)_2](BAr^F{}_4)$ affords deep red crystals of $[(\mu_2\text{-}Ga)_2Pd_3(GaCp^*)_6](BAr^F)_2$ (**3**$(BAr^F{}_4)_2$), as the major product (Figure 2).

The dication **3**[15] is the very first example of a metal complex or cluster containing more than one substituent-free Ga^+ ligand. The quality of the single-crystal structure obtained does not allow the discussion of the bond lengths

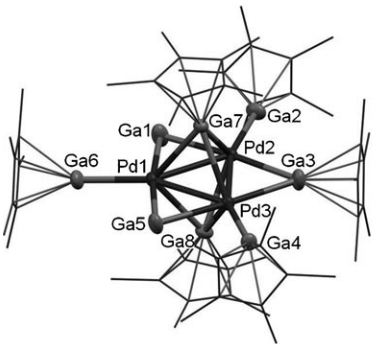


Figure 2. Molecular structure of the cation **3** in the solid state (hydrogen atoms and anions are omitted for clarity). The substituent-free Ga$^+$ ligands are denoted as Ga1 and Ga5.

and angles in detail. Nevertheless the overall composition and the structural features of the Pd$_3$Ga$_8$ core have been unambiguously established from the available data and the refinement. The similarity of **3** to the mono cation **2** is striking. The structure of **3** is simply derived by attaching a second Ga$^+$ to the free, not bridged edge of a hypothetical Pd analogue of **2**. Thus, the triangular Pd$_3$ unit of **3** is capped by two μ$_3$-GaCp* ligands, a terminal GaCp* is on each palladium the three Pd–Pd edges are bridged by one GaCp* unit and two naked Ga$^+$ moieties. ^{1}H NMR experiments indicate a fluxional structure of this complex in solution: Four distinct signals at 25 °C ($\delta =$ 2.01, 1.93, 1.84, 1.74 ppm) arising from the two equivalent terminal GaCp* units (Ga2 and Ga4), the triply bridging GaCp* units (Ga7 and Ga8), the terminal GaCp* unit (Ga6) between the two substituent-free Ga$^+$, and the doubly bridging GaCp* (Ga3) ligands, respectively, coalesce to one broad signal at 75 °C ($\delta = 2.10$ ppm).

In summary, the synthesis of **1–3** is a significant step forward in the chemistry of sparsely explored naked Ga$^+$ moieties. Terminal,[5] linear bridging,[6] and now bent edge-bridging coordination modes of Ga$^+$ have been found. Other multiply charged cluster cations similar to **3** and beyond, bearing more than one Ga$^+$ unit in a bridging or even interstitial position may be accessible as well.[17] On pursuing our goal to rationally synthesize larger metal-rich molecules as models or precursors for the respective intermetallic phases,[2–6,16] the selective reduction of cations such as **1–3** back to neutral species, without the loss of the original M$_a$E$_b$ core will be the next challenge.

Received: October 21, 2009

Keywords: carbenoids · cluster compounds · gallium · Group 13 elements · oxidation state

---

[1] a) P. W. Roesky, *Dalton Trans.* **2009**, 1887–1893; b) H.-J. Himmel, G. Linti, *Angew. Chem.* **2008**, *120*, 6425–6427; *Angew. Chem. Int. Ed.* **2008**, *47*, 6326–6328; c) D. L. Kays, S. Aldridge, *Struct. Bonding (Berlin)* **2008**, *130*, 29–122; d) R. J. Baker, C. Jones, *Coord. Chem. Rev.* **2005**, *249*, 1857–1869; e) C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R. A. Fischer, *Eur. J. Inorg. Chem.* **2004**, 4161–4176; f) G. Linti, H. Schnöckel, *Coord. Chem. Rev.* **2000**, *206–207*, 285–319; g) R. A. Fischer, J. Weiss, *Angew. Chem.* **1999**, *111*, 3002–3022; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830–2850.

[2] a) M. Cokoja, H. Parala, M.-K. Schroeter, A. Birkner, M. W. E. van den Berg, W. Grünert, R. A. Fischer, *Chem. Mater.* **2006**, *18*, 1634–1642; b) M. Cokoja, H. Parala, A. Birkner, O. Shekhah, M. W. E. van den Berg, R. A. Fischer, *Chem. Mater.* **2007**, *19*, 5721–5733; c) R. A. Fischer, D. Weiss, M. Winter, I. Müller, H. D. Kaesz, N. Froehlich, G. Frenking, *J. Organomet. Chem.* **2004**, *689*, 4611–4623; d) D. Weiß, M. Winter, K. Merz, A. Knüfer, R. A. Fischer, N. Fröhlich, G. Frenking, *Polyhedron* **2002**, *21*, 535–542; e) B. Fraser, L. Brandt, W. K. Stovall, H. D. Kaesz, S. I. Khan, F. Maury, *J. Organomet. Chem.* **1994**, *472*, 317–328; f) R. A. Fischer, H. D. Kaesz, S. Khan, H.-J. Müller, *Inorg. Chem.* **1990**, *29*, 1601–1602.

[3] M. Cokoja, H. Parala, M. K. Schroeter, A. Birkner, M. W. E. van den Berg, K. V. Klementiev, W. Grünert, R. A. Fischer, *J. Mater. Chem.* **2006**, *16*, 2420–2428.

[4] a) T. Cadenbach, C. Gemel, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 9286–9289; *Angew. Chem. Int. Ed.* **2008**, *47*, 9146–9149; b) T. Cadenbach, T. Bollermann, C. Gemel, I. Fernandez, M. von Hopffgarten, G. Frenking, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 9290–9295; *Angew. Chem. Int. Ed.* **2008**, *47*, 9150–9154.

[5] B. Buchin, C. Gemel, T. Cadenbach, I. Fernandez, G. Frenking, R. A. Fischer, *Angew. Chem.* **2006**, *118*, 5331–5334; *Angew. Chem. Int. Ed.* **2006**, *45*, 5207–5210.

[6] T. Cadenbach, C. Gemel, R. Schmid, M. Halbherr, K. Yusenko, M. Cokoja, R. A. Fischer, *Angew. Chem.* **2009**, *121*, 3930–3934; *Angew. Chem. Int. Ed.* **2009**, *48*, 3872–3876.

[7] a) P. Jutzi, B. Neumann, L. O. Schebaum, A. Stammler, H.-G. Stammler, *Organometallics* **1999**, *18*, 4462–4464; b) C. Gemel, T. Steinke, D. Weiss, M. Cokoja, M. Winter, R. A. Fischer, *Organometallics* **2003**, *22*, 2705–2710.

[8] Crystal structure analysis of **1**BAr$^F{}_4$: crystal size $0.26 \times 0.24 \times 0.20$ mm^3, monoclinic, space group $P2_1/c$, $a = 19.5708(5)$, $b = 15.4373(4)$, $c = 25.3173(6)$ Å, $\beta = 95.153(2)°$, $V = 7618.0(3)$ Å^3, $Z = 4$, $\sigma_{\text{calcd}} = 1.579$ g cm^{-3}, $\Theta_{\min} = 2.76$ $\Theta_{\max} = 25.00$, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $T = 108(2)$ K. 38626 reflections (13378 unique) were measured on a Oxford Excalibur 2 diffractometer [R(int) = 0.0449]. The structural solution and refinement were carried out by using the programs SHELXS-97 and SHELXL-97.[18] Final values for R1 and $wR2(F2)$: 0.0423 and 0.1088 (all data). CCDC 6751563 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. Owing to disordered solvent the the X-ray data were corrected employing the SQUEEZE routine in PLATON.[19]

[9] T. Cadenbach, C. Gemel, T. Bollermann, I. Fernandez, G. Frenking, R. A. Fischer, *Chem. Eur. J.* **2008**, *14*, 10789–10796.

[10] T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Chem. Eur. J.* **2005**, *11*, 1636–1646.

[11] Crystal structure analysis of **2**BAr$^F{}_4$: crystal size $0.20 \times 0.15 \times 0.13$ mm^3, monoclinic, space group Pm, $a = 14.506(6)$, $b = 14.886(11)$, $c = 14.840(6)$ Å, $\beta = 92.37(3)°$, $V = 3201(3)$ Å^3, $Z = 1$, $\sigma_{\text{calcd}} = 1.425$ gcm^{-3}, $\Theta_{\min} = 3.03$, $\Theta_{\max} = 27.00$, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $T = 104(2)$ K. 29071 reflections (12427 unique) were measured on a Oxford Excalibur 2 diffractometer [R-(int) = 0.0925]. The asymmetric unit consists of half of the cation and anion, respectively with the mirror plane of the cation located in the Pt$_3$Ga$_5$ plane. The structural solution and refinement were carried out by using the programs SHELXS-97 and SHELXL-97.[18] Final values for $R1$ and $wR2(F^2)$: 0.1021 and 0.1572 (all data). Note that the vibrational ellipsoids of Ga5 and Ga3 are a bit large. Care must be taken comparing the respective Pt-Ga distances. CCDC 751562 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.

[12] a) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311–319; b) K. Wade, *J. Chem. Soc. D* **1971**, 792–793.

[13] M. J. D'Aniello, Jr., C. J. Carr, M. G. Zammit, *Inorg. Synth.* **1989**, *26*, 319–323.

[14] K. H. Dahmen, D. Imhof, L. M. Venanzi, *Helv. Chim. Acta* **1994**, *77*, 1029–1036.

[15] Crystal structure analysis of **3**$(\mathrm{BAr^F}_4)_2$: crystal size $0.40 \times 0.38 \times 0.35$ mm^3, monoclinic, space group $P2_1/c$, $a = 17.8274(5)$, $b = 29.7226(8)$, $c = 32.4847(9)$ Å, $\beta = 123.284(1)°$, $V = 14389.3(7)$ Å^3, $Z = 4$, $\sigma_{\mathrm{calcd}} = 1.576$ g cm^{-3}, $\Theta_{\mathrm{min}} = 2.97$, $\Theta_{\mathrm{max}} = 25.00$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $T = 104(2)$ K. 166955 reflections (25286 unique) were measured on a Oxford Excalibur 2 diffractometer [$R(\mathrm{int}) = 0.1109$]. The structural solution and refinement were carried out using the programs SHELXS-97 and SHELXL-97.[18] Final values for $R1$ and $wR2(F^2)$: 0.1531 and 0.2567 (all data). Note that the vibrational ellipsoids of Ga6 and Ga3 are a bit large. Care must be taken comparing the respective Pt–Ga distances. CCDC 751564 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.

[16] a) M. Li, C. R. Li, F. M. Wang, W. J. Zhang, *Intermetallics* **2006**, *14*, 826–831; b) W. X. Yuan, Z. Y. Qiao, H. Ipser, G. Eriksson, *J. Phase Equilib. Diffus.* **2004**, *25*, 68–74; c) C. Wannek, B. Harbrecht, *J. Alloys Compd.* **2001**, *316*, 99–106.

[17] One reviewer pointed out that the cations **2** and **3** should either be defined as Ga/GaCp coordinated clusters or called clusters exhibiting special Ga atoms, as they are also observed in metalloid $\mathrm{Ga}_n\mathrm{R}_m$ clusters (see for example: H. Schnöckel, *Dalton Trans.* **2008**, 4344–4362). We prefer to choose the description as Ga/GaCp coordinated clusters.

[18] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, **1997**; G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

[19] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.