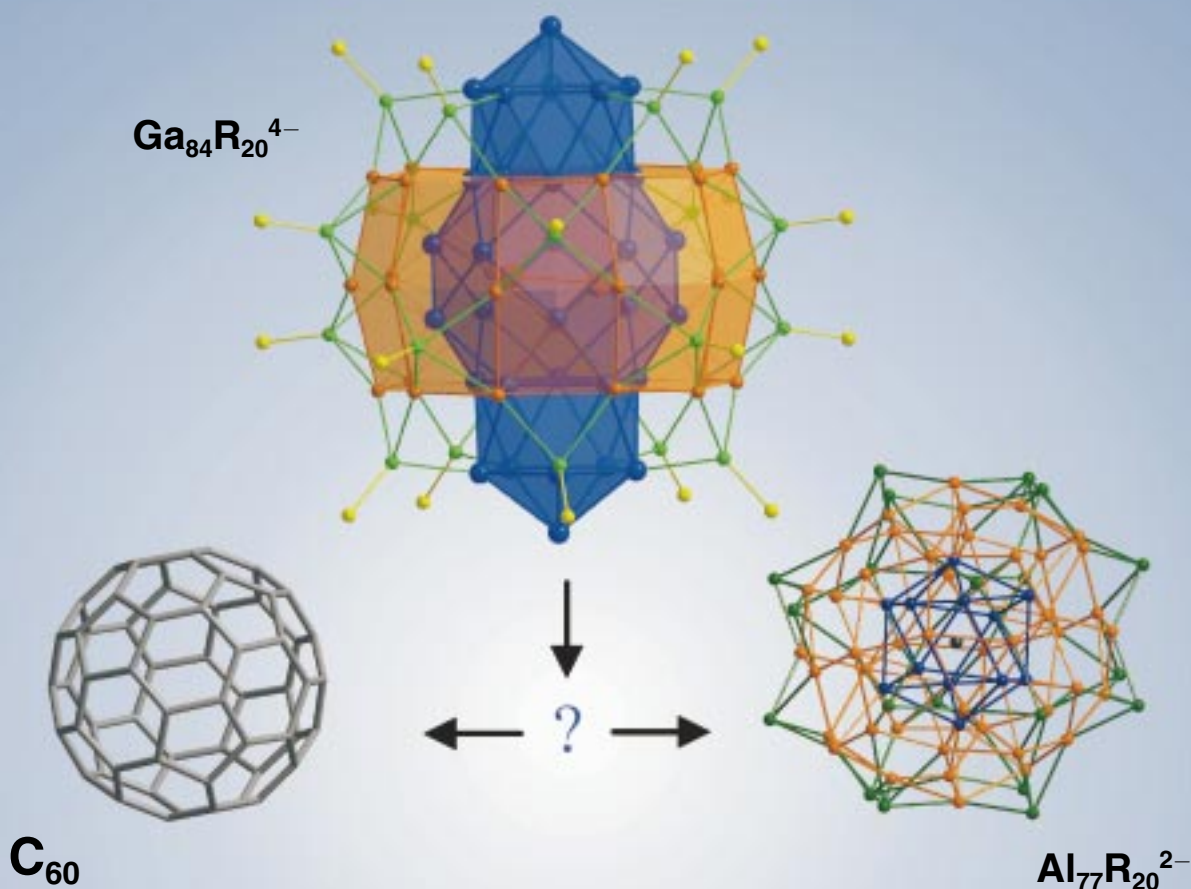


# The surprising geometry of a $\text{Ga}_{84}\text{R}_{20}^{4-}$ cluster ( $\text{R} = \text{N}(\text{SiMe}_3)_2$ ) ...

- 64 “naked” Ga atoms, free of ligands, representing a new world record in the area of cluster research
- a  $\text{Ga}_2$  unit in the center surrounded by a cigar-shaped  $\text{Ga}_{32}$  skeleton, with a central Ga-Ga separation close to that of the shortest known Ga-Ga bonds (“triple bond”)



... points to bonding properties,

which are intermediate between the class of **polyhedral clusters** with covalent bonds, the most prominent representatives being the fullerenes, and the typical **metalloid clusters**, such as the  $\text{Pd}_{145}$  and the  $\text{Al}_{77}\text{R}_{20}^{2-}$  clusters.

# Synthesis and Structure of a $\text{Ga}_{84}\text{R}_{20}^{4-}$ Cluster— A Link between Metalloid Clusters and Fullerenes?\*

Andreas Schnepf und Hansgeorg Schnöckel\*

*Dedicated to Professor Anthony J. Downs  
on the occasion of his 65th birthday*

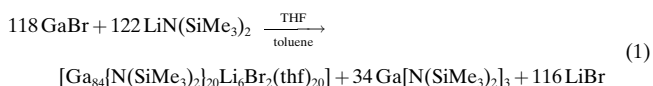
Metalloid clusters,<sup>[1, 8]</sup> that is molecular metal clusters in which the number of direct metal–metal contacts exceeds that of the metal–ligand bonds, have been intensively studied worldwide for many years because of the potential of clusters of this type, for example, in the area of molecular electronics.<sup>[2]</sup> The most prominent and most widely used species of this type is the  $\text{Au}_{55}$  cluster,<sup>[2]</sup> although for this and for similar species, and in some cases larger Pd and Pt clusters, only structural information based on modern microscopic techniques is available.<sup>[2]</sup> The largest metalloid precious metal cluster, characterized by diffraction, contains 59 Pd atoms,<sup>[3]</sup> of which only 11 are “naked”, that is do not form ligand interactions. Thus, the structural elucidation of an  $\text{Al}_{77}$  cluster with 57 “naked” Al atoms by our group three years ago was surprising and shows the progress in the syntheses of these cluster compounds with regard to earlier processes.<sup>[4]</sup> To understand the formation of this  $\text{Al}_{77}$  cluster, which can be interpreted as an intermediate on the pathway from metastable  $\text{Al}^{\text{I}}$  compounds prepared cryochemically<sup>[5]</sup> to Al metal and to  $\text{AlR}_3$ , we have tried to trap further intermediates on the pathway to the  $\text{Al}_{77}$  cluster under very mild reaction conditions over the last few years. With the same ligand,  $\text{N}(\text{SiMe}_3)_2$ , the number of Al atoms per cluster could be changed and compounds which contain 7,<sup>[1]</sup> 12,<sup>[6]</sup> 14,<sup>[7]</sup> and finally 77 Al atoms could be obtained by varying the reaction temperature alone. In each of these clusters structural elements are present which are characteristic for aluminum as a typical metal, that is these clusters are in fact similar to metals, thus metalloid.<sup>[1, 8]</sup>

Parallel to these experiments we started to produce analogous Ga clusters, since, owing to the variety of the solid-state modifications of gallium—exhibiting in some cases covalently bonded units,<sup>[9]</sup> which are reminiscent of bonding modes displayed by boron—other structures and bonding situations are expected than those found in Al clusters.

Following our successful synthesis of a  $\text{Ga}_{19}$ <sup>[8]</sup> and a  $\text{Ga}_{22}$  cluster<sup>[10]</sup> and the recent description of a  $\text{Ga}_{22}$ <sup>[11]</sup> and a  $\text{Ga}_{26}$  cluster,<sup>[12]</sup> we report herein on a  $\text{Ga}_{84}$  cluster with 64 “naked” Ga atoms. This surpasses the  $\text{Al}_{77}$  cluster as the largest structurally characterized metalloid cluster in the entire field of metal atom clusters and displays a totally unexpected

structure in comparison to the  $\text{Al}_{77}$  cluster despite the same number and type of ligands.

The reaction of a metastable GaBr solution in toluene/THF (4/1), which was obtained by the cocondensation of the GaBr molecules—generated at about 1000 °C—in a toluene/THF solvent mixture,<sup>[5]</sup> with a solution of  $\text{LiN}(\text{SiMe}_3)_2$  gives black, metallic, shiny crystals of the composition  $[\text{Ga}_{84}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{4-}$  (**1a**) after warming to 55 °C. The reaction proceeded according to Equation (1).



Only the listed products were generated and no elemental gallium was formed. The quality and size of the crystals (up to  $1.5 \times 1.5 \times 0.5$  mm), which were thermally stable up to about 400 °C, allow a precise determination of the structure and open the way to studies of the physical properties (in progress). In the crystal structures the anionic  $\text{Ga}_{84}$  units  $[\text{Ga}_{84}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{4-}$  (**1a**) (Figure 1) adopt a slightly distorted, cubic closest packing, in which the tetrahedral holes are completely occupied by  $[\text{Li}(\text{thf})_4]^+$  ions and the octahedral holes with the dication  $[(\text{thf})_3\text{LiBrLi}(\text{thf})_3]^{2+}$ .

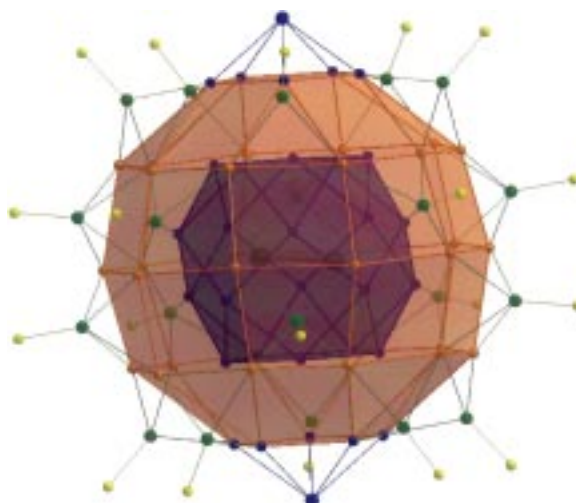


Figure 1. Molecular structure of  $[\text{Ga}_{84}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{4-}$  (**1a**) in shell representation (without  $\text{SiMe}_3$  groups).

Compound **1a** contains 84 Ga atoms, whereas in the corresponding Al cluster only 77 Al atoms are present in the analogous ligand shell of 20  $\text{N}(\text{SiMe}_3)_2$  groups. This finding appears plausible, as Ga–Ga bonds, for example in  $\text{R}_2\text{M}–\text{MR}_2$  ( $\text{M} = \text{Al}, \text{Ga}$ ;  $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ), are about 4.5 % shorter than Al–Al bonds.<sup>[13]</sup> In the shell-like representation of **1a** (Figure 1), which was chosen analogously to that of the  $\text{Al}_{77}$  cluster, Ga–Ga distances have to be taken into account up to 368 pm (sum of the van der Waals radii 380 pm), that is, in this representation, a similarity to the  $\text{Al}_{77}$  cluster is only feigned. The difference between the  $\text{Al}_{77}$  cluster and **1a** becomes particularly clear on comparison of the coordination numbers: Whereas the coordination numbers for the  $\text{Al}_{77}$  cluster decrease from the center outwards from 12 through

[\*] Prof. Dr. H. Schnöckel, Dr. A. Schnepf  
Institut für Anorganische Chemie der Universität Karlsruhe (TH)  
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe (Germany)  
Fax: (+49) 721-608-4854  
E-mail: hg@achpc9.chemie.uni-karlsruhe.de

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8 to 6, a small coordination number of only 4 has been noted for the inner shell of the  $\text{Ga}_{84}$  cluster, which increases to 8 in the next shell and subsequently decreases again to 4 further out. A different view of the bonding characteristics of the  $\text{Ga}_{84}$  cluster that focuses on the geometry of the 64 “naked” Ga atoms (Figure 2) appears better than this shell-like representation.

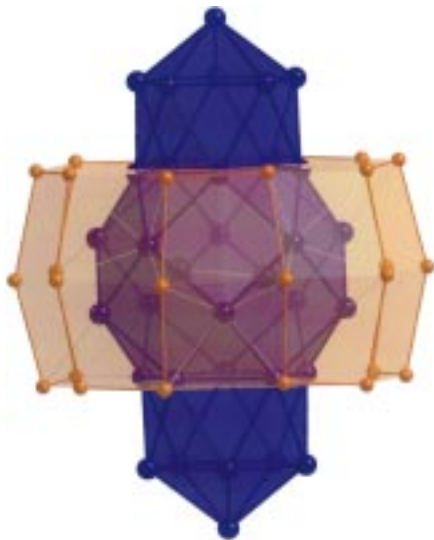


Figure 2. Polyhedral representation of the 64 gallium atoms not bound to one ligand. Ga–Ga distances (min./mean/max.) in the tube-shaped  $\text{Ga}_{32}$  unit: 262.8(2)/274.3/288.7(2) Å.

Notably, the Ga–Ga bond in the central  $\text{Ga}_2$  group ( $d(\text{Ga–Ga}) = 235$  pm) is as short as that of the so-called triple bond<sup>[14]</sup> and the (blue) tube- or football-like  $\text{Ga}_{32}$  unit in which the mean Ga–Ga distance is only 278 pm. Here the  $\text{Ga}_{20}$  unit from Figure 1 is supplemented with two icosahedral  $\text{Ga}_6$  caps, which according to the schematic shell model in Figure 1 should be assigned to the orange-colored shell. However, due to the significantly shorter distances to the  $\text{Ga}_{20}$  group, these  $\text{Ga}_6$  caps are better assigned to the blue unit in Figure 1. The resulting  $\text{Ga}_{32}$  unit is surrounded by a further 30 “naked” Ga atoms, which wind around the  $\text{Ga}_{32}$  group with Ga–Ga distances in the following sequence: 273 pm (horizontally), 293 pm (vertically), 293 pm (vertically) and so on. These 30 Ga atoms form three planar  $\text{Ga}_{10}$  rings with in some cases very weak Ga–Ga bonds. This arrangement of naked Ga atoms is unique in the field of molecular compounds.

In contrast, in the solid-state structures of elemental gallium the structure of  $\alpha$ -Ga with the unusual  $\text{Ga}_2$ -dumbbell ( $d(\text{Ga–Ga}) = 245$  pm) and the structure of  $\delta$ -Ga with strongly distorted icosahedral  $\text{Ga}_{12}$  units (275–289 pm) show structural relationships with **1a**. As each of the coordination numbers in **1a** is lower than in the above-mentioned Ga element modifications (if only the bond lengths up to 289 pm are taken into account), the bonding in **1a** must be significantly more covalent. This consideration shows that **1a** has a topology in the environment of the  $\text{Ga}_{32}$  units that is similar to the more covalent bonding in the boranes or in the element structure of boron, and can partly be considered to be on the path to fullerenes.<sup>[15]</sup> This somewhat bold relationship is based

on the fact that the  $\text{Ga}_{32}$  unit is a hollow body (apart from the central  $\text{Ga}_2$  dumbbell) that only displays short distances of 276 pm (mean) to the three external  $\text{Ga}_{10}$  rings. This picture of a predominantly covalent partial structure of the  $\text{Ga}_{32}$  group is supported by the  $\text{Ga}_2$  unit with an especially short Ga–Ga distance of 235 pm situated in the center of the  $\text{Ga}_{84}$  cluster, as endohedral species of fullerenes with, for example,  $\text{Sc}_2$ <sup>[16]</sup> and even larger units (e.g.  $\text{Sc}_3\text{N}$ <sup>[17]</sup>) have also been synthesized very recently. In contrast to the fullerenes, **1a** represents to our knowledge a unique situation in the entire field of molecular species: An  $\text{M}_2$  “molecule” is situated in a cage of 20 (or 32) atoms of the same metal. In contrast, a  $\text{Sc}_2$  “molecule” in a  $\text{C}_{84}$  cage of nonmetal atoms is found in the above-mentioned endohedral fullerenes. There are numerous structural features of **1a** which point towards analogies with both the fullerenes and with the  $\text{Al}_{77}$  cluster, such that with respect to its structure, **1a** lies between both extremes. In accord with this classification of the bonding in the  $\text{Ga}_{84}$  cluster being between that in the  $\text{Al}_{77}$  cluster and that in the fullerenes, in the following a distinction should be made to the metalloid precious metal clusters.

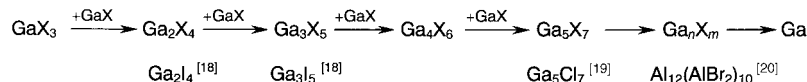
Both the experimental findings, based on microscopic methods, as well as theoretical considerations for these metalloid cluster groups generally lead to the result that the geometry of the metal atoms represents a section of the crystalline metal.

In contrast, our results for the shell-like  $\text{Al}_{77}$  cluster show that this view should be evaluated very critically. Evidently, the ligands and their bonding to the outer metal atoms play a decisive role in the formation of the cluster. In the case of the  $\text{Al}_{77}$  cluster, the coordination number 12 expected for the close packing is only found for the central Al atom; here also the ideal anticuboctahedral arrangement is not realized. The coordination numbers and the bond lengths decrease on moving to the outer shells, that is the bonding characteristics become more “molecular”. This view of metalloid, ligand-protected clusters is also supported by our results for **1a**: In the center of the cluster, the coordination numbers and building blocks are typical, for example, for  $\alpha$ - and  $\delta$ -gallium (dumbbell, icosahedra), whereas the outer-lying Ga–Ga bonds are more “molecular”, that is have distances similar to those in  $\text{R}_2\text{GaGaR}_2$  or  $\text{Ga}_4\text{R}_4$  units.

Furthermore, the formation of crystalline compounds for the  $\text{Al}_{77}$  and for the  $\text{Ga}_{84}$  clusters contradicts the tendency of the precious metal cluster compounds not to crystallize. This difference is plausible since here the stabilizing ligand shell is bound rigidly by 2e-2c bonds ( $\text{AlN}$  or  $\text{GaN}$ ) to particular metal atoms. In contrast, transition metal clusters show a more flexible ligand shell through  $\sigma$ -donor and  $\pi$ -acceptor bonds (e.g.  $\text{CO}$ ,  $\text{PR}_3$  and  $\text{SR}_2$ ) with in some cases bridging properties, which leads to stationary equilibria, in which many species that differ only slightly in terms of energy probably exist. Consequently, a high enough concentration of a distinct species, which is necessary for the formation of crystalline samples, is only obtained rarely.

The mechanism of formation of the Al and Ga clusters is also probably completely different. The principle of disproportionation is decisive; for reactive species such as  $\text{MX}$  ( $\text{M} = \text{Al, Ga}$ ;  $\text{X} = \text{halogen or organic substituent}$ ) it proceeds so

slowly at low temperatures that intermediates can be trapped before the thermodynamically stable bulk metal and the  $M^{III}$  species (e.g.  $3MX \rightarrow 2M_{solid} + MX_3$ ) are finally formed. Through gradual insertion of MX units (excess) and elimination of  $MX_3$  (or  $M_2X_4$ ), cluster growth occurs (Scheme 1) which can be influenced by the choice of temperature, donor, halide, and the organic group.



Scheme 1. Growth of  $Ga_nX_m$  clusters (X = halogen) by insertion of GaX and elimination of  $GaX_3$  or  $Ga_2X_4$  units.

Thus, in the same chemical environment an  $Al_7$ ,  $Al_{12}$ ,  $Al_{14}$ , or  $Al_{77}$  cluster can be obtained simply by variation of the temperature alone. The last step, the formation of the metal, only occurs if a critical cluster size is reached (e.g., by warming the solution to 100 °C) in the reducing atmosphere (MX excess); that is, a giant cluster is produced whose metal core is largely equivalent to the bulk material and which can disproportionate into metal and  $M^{III}$  species without large changes in the bonding.<sup>[21]</sup>

The results presented here on a  $Ga_{84}$  cluster show that such disproportionations of reactive species also lead to success in systems that are outside the regime of typical metals and consequently lead to unusual cluster structures with predominantly covalently bonded units. Thus gentle disproportionation appears to be a successful synthesis concept for a diverse range of cluster compounds. For such compounds, for example, the analogous fullerenes,<sup>[22]</sup> special properties, for example, with regard to the electrical conductivity are expected. In this respect, interesting effects can be expected already from the arrangement of the  $Ga_{84}$  units in the crystal (Figure 3); the  $Ga_{84}$  clusters are each separated by only two

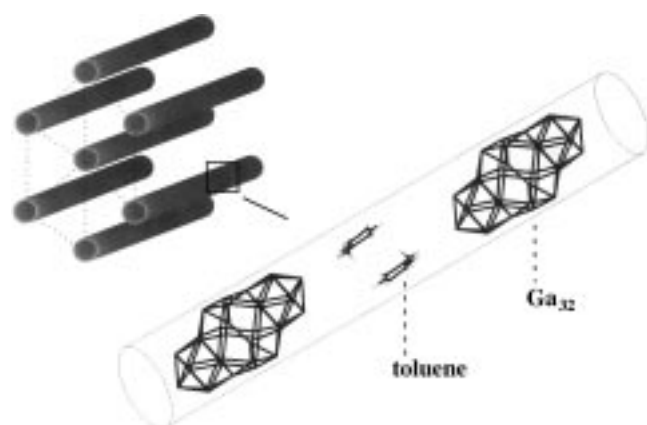


Figure 3. Arrangement of the  $Ga_{84}$  cluster in the crystal. For clarity only the  $Ga_{32}$  subunits are presented.

toluene molecules that are located over the “naked” apex atoms, leading to the formation of “tubes” of  $Ga_{84}$  clusters. Seen from the front (Figure 3), these “tubes” form a distorted hexagonal arrangement of pipes, which are separated from one another by the ligand shell. Now that we are in the position to synthesize sufficient amounts of **1** in crystalline

form, we have started conductivity measurements which are problematic due to the sensitivity of the crystals. If, as hoped, we find special physical properties of **1** (e.g. superconductivity as in the fullerenes), the interest in the  $Ga_{84}$  cluster in the interdisciplinary fields of chemistry, physics, and material sciences should increase rapidly and stimulate further efforts in the synthesis of these metalloid clusters.

## Experimental Section

$LiN(SiMe_3)_2$  (1.8 g, 10 mmol) was added to toluene (30 mL) and cooled to  $-78^\circ\text{C}$ . A GaBr solution (27 mL, 8.3 mmol of a 0.3 M solution in toluene/THF (3:1)) was added to this suspension slowly at  $-78^\circ\text{C}$  with a steel cannula. The mixture was slowly brought to room temperature under stirring, and an almost black solution was

obtained. This was warmed to  $55^\circ\text{C}$  for 20 h. After the mixture had been cooled to room temperature, black rhombic crystals of **1** (220 mg, 0.02 mmol, 38 %) were obtained on the glass wall.

Crystal structure data of **1**:  $[Ga_{84}[N(SiMe_3)_2]_{20}][Li(thf)_4]_2[Li_2Br(thf)_6]_2 \cdot 2$  toluene,  $M_r = 10892.17$ , Crystal dimensions  $0.2 \times 0.3 \times 0.4$  mm, triclinic, space group  $P\bar{1}$ ,  $a = 24.724(5)$ ,  $b = 25.849(5)$ ,  $c = 39.019(8)$  Å,  $\alpha = 88.95(3)^\circ$ ,  $\beta = 71.65(3)^\circ$ ,  $\gamma = 62.30(3)^\circ$ ,  $V = 20712.5(72)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.746$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 5.703$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 47.88^\circ$ , 128094 measured reflections, 60258 independent reflections ( $R_{\text{int}} = 0.0832$ ), absorption correction: numerical (min./max. transmission 0.1454/0.4062),  $R_1 = 0.0523$ ,  $wR_2 = 0.1451$ . Stoe-IPDS diffractometer (MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), 200 K). The structure of **1** was solved by direct methods with SHELXS and SHELXTL (G. M. Sheldrick, Universität Göttingen) and refined against  $F^2$  for all observed reflections. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1343228. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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- [1] A. Purath, R. Köppe, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3114; *Angew. Chem. Int. Ed.* **1999**, *38*, 2926.
- [2] a) *Cluster and Colloids* (Ed.: G. Schmid), VCH, Weinheim, **1994**; b) P. Braunstein, L. A. Oro, P. R. Raithby, *Metal Clusters in Chemistry*, Wiley-VCH, Weinheim, **1999**.
- [3] N. T. Tran, M. Kawano, D. R. Powell, L. F. Dahl, *J. Am. Chem. Soc.* **1998**, *120*, 10986. A recent paper about a  $Pd_{145}$  cluster could not be considered since this first appeared as a VIP paper after the correction of the paper; N. T. Tran, D. R. Powell, L. F. Dahl, *Angew. Chem.* **2000**, *112*, 4287; *Angew. Chem. Int. Ed.* **2000**, *39*, 4121.
- [4] A. Ecker, E. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379.
- [5] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129.
- [6] A. Purath, R. Köppe, H. Schnöckel, *Chem. Commun.* **1999**, 1933.
- [7] H. Köhnlein, G. Stöber, E. Baum, E. Möllhausen, U. Huniar, H. Schnöckel, *Angew. Chem.* **2000**, *112*, 828; *Angew. Chem. Int. Ed.* **2000**, *39*, 799.
- [8] A. Schnepf, G. Stöber, H. Schnöckel, *J. Am. Chem. Soc.* **2000**, *122*, 9178.
- [9] U. Häußermann, S. I. Simak, R. Ahuja, B. Johansson, *Angew. Chem.* **2000**, *112*, 1301; *Angew. Chem. Int. Ed.* **2000**, *39*, 1246.
- [10] A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3578; *Angew. Chem. Int. Ed.* **1999**, *38*, 3381.
- [11] G. Linti, A. Rodig, *Chem. Commun.* **2000**, 127, 2000.
- [12] A. Rodig, G. Linti, *Angew. Chem.* **2000**, *112*, 3076; *Angew. Chem. Int. Ed.* **2000**, *39*, 2952.
- [13] Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *Organometallics* **1999**, *18*, 584, 94.
- [14] a) J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471; b) R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1095; c) F. A. Cotton, A. H. Cowley, X. Feng, *J. Am.*



- Chem. Soc.* **1998**, 120, 1795; d) J. Grunenberg, N. Goldberg, *J. Am. Chem. Soc.* **2000**, 122, 6045.
- [15] Other compounds, which at first glance appear similar, such as the fullerene-analogous  $\text{In}_{74}$  in the Zintl phase  $\text{Na}_{96}\text{In}_{77}\text{Ni}_{12}$  are fundamentally different to the metalloid clusters: In such Zintl phases<sup>[23]</sup> the metallic structure of the metals is broken by reduction with electro-positive elements, resulting in negatively charged cluster units containing negative average oxidation numbers. In contrast, the molecular metalloid cluster intermediates lie on the path from monomeric or oligomeric oxidized species to the metals, that is, the average oxidation numbers for example within the metalloid Ga clusters are between +1 and 0.
- [16] M. Inakuma, E. Yamamoto, T. Kai, C.-R. Wang, T. Tomiyama, H. Shinohara, T. J. S. Dennis, M. Hulmann, M. Krause, H. Kuzmany, *J. Phys. Chem. B* **2000**, 104, 5072.
- [17] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Amstead, *Nature* **1999**, 401, 55.
- [18] A. Schnepf, C. Doriat, E. Möllhausen, H. Schnöckel, *Chem. Commun.* **1997**, 2111.
- [19] D. Loos, H. Schnöckel, D. Fenske, *Angew. Chem.* **1993**, 105, 1124; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1059.
- [20] C. Klemp, R. Köppe, E. Weckert, H. Schnöckel, *Angew. Chem.* **1999**, 111, 1852; *Angew. Chem. Int. Ed.* **1999**, 38, 1740.
- [21] The Al and Ga cluster compounds that we have already structurally characterized show that the bulkiness of the ligand has an effect on the maximum cluster size, that is for clusters with the same number of ligands a bulky ligand leads to a smaller metal cluster than a less bulky ligand. Indirectly, this principle becomes clear on comparing the  $\text{Ga}_{84}$  cluster with the  $\text{Al}_{77}$  cluster, which is surrounded by the same ligand shell (see above). Analogous conclusions regarding the influence of the ligands can not yet be drawn for the metalloid precious metal clusters, since for the larger clusters hardly any detailed structure information is available due to the lack of single-crystal structure determinations.
- [22] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, A. R. Kortan, *Nature* **1991**, 350, 600.
- [23] J. D. Corbett, *Angew. Chem.* **2000**, 112, 682; *Angew. Chem. Int. Ed.* **2000**, 39, 692.

## **$[\{\text{Rh}(\eta^5\text{-Ph}_2\text{C}_2\text{B}_9\text{H}_9)(\mu_3\text{-OH})\}_4]$ : A Tetrameric Icosahedral Metallocarborane Containing an $\{\text{Rh}(\text{OH})\}_4$ Cubane Cluster\*\***

Bruce E. Hodson, David Ellis, Thomas D. McGrath, John J. Monaghan, Georgina M. Rosair, and Alan J. Welch\*

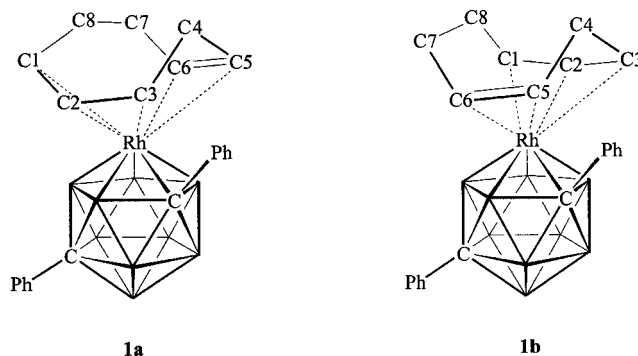
We are currently investigating the mechanism of isomerization of metallocarboranes by inducing low-temperature isomerizations through steric crowding.<sup>[1]</sup> Our strat-

egy uses vertex-substitution to follow the movement of specific cluster vertices through the isomerization process since the integrity of the vertex-substituent bond is reasonably assured at low temperatures and thus eventually should provide a complete experimental mapping of the process. Although our initial studies have involved platina-,<sup>[2]</sup> molybda-,<sup>[3]</sup> and nickeladiphenylcarboranes<sup>[4]</sup> we have begun to investigate rhodium species. This has led, fortuitously, to the isolation and characterization of the novel rhodacarborane tetramer described herein.

When  $\text{Na}_2[7,8\text{-Ph}_2\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_9]$  (prepared in situ from  $[\text{HNet}_3][7,8\text{-Ph}_2\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]$  and excess NaH in THF under reflux) is allowed to react with  $[\{\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}\}_2]$  in THF, two new compounds are formed which may be separated by chromatography. The major species **1**, is

$[1,8\text{-Ph}_2\text{-}2\text{-(}1\text{-}3\text{-}\eta^3\text{-}5,6\text{-}\eta^2\text{-C}_8\text{H}_{11}\text{)-}closo\text{-}2,1,8\text{-RhC}_2\text{B}_9\text{H}_9]$  **1**

characterized by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy and by a crystallographic study. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **1** contains eleven peaks instead of the expected nine between  $\delta = +10$  and  $-15$ , the range usually associated with resonance signals from *closo* metallocarboranes. This apparent anomaly was resolved by analysis of  $^1\text{H}$ ,  $^1\text{H}\text{-}^1\text{H}$  correlated (COSY), and  $^1\text{H}\text{-}^1\text{H}$  nuclear Overhauser effect (nOe) NMR spectra, which show clear evidence for two conformers (**1a** and **1b**, Scheme 1) which differ in the disposition of the  $\eta^3\text{:}\eta^2\text{-C}_8\text{H}_{11}$  ring relative to the carborane cage. Unfortunately it is not possible to establish which conformer is the major component in solution. Subsequent exhaustive thin layer chromatography (tlc) with a variety of eluents could not separate **1a** and **1b**.



Scheme 1. The two conformers of compound **1**. The relative amounts of **1a**:**1b** are approximately 3:1 in the solid state (by X-ray diffraction). In solution (by NMR) there are also two conformers in a 3:1 ratio, but it is not possible to establish which is the major form.

A structural study of **1**<sup>[5]</sup> (Figure 1) establishes that low-temperature isomerization has occurred, separating the cage carbon atoms in a net  $1,2 \rightarrow 1,7$  manner<sup>[1]</sup> as in *closo-C*<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. In the crystal the  $\eta^3\text{:}\eta^2\text{-C}_8\text{H}_{12}$  ligand is partially disordered (atoms C23 and C25) corresponding to an effective superimposition of conformers **1a** and **1b** in the approximate ratio 3:1.

The direct synthesis of compound **1** is unexpected. Jeffery et al.<sup>[6]</sup> have previously obtained the related (but nonisomerized) species  $[1,2\text{-Me}_2\text{-}3\text{-(}1\text{-}3\text{-}\eta^3\text{-}5,6\text{-}\eta^2\text{-C}_8\text{H}_{11}\text{)-}closo\text{-}3,1,2\text{-}$

[\*] Prof. A. J. Welch, B. E. Hodson, Dr. D. Ellis, Dr. T. D. McGrath, Dr. G. M. Rosair  
Department of Chemistry  
Heriot-Watt University  
Edinburgh EH14 4AS (UK)  
Fax: (+44) 131-451-3180  
E-mail: a.j.welch@hw.ac.uk  
Prof. J. J. Monaghan  
Department of Chemistry, University of Edinburgh (UK)

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