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$[\mathrm{Li(thf)}_4]_2^{\;+}[\mathrm{Ga}_{12}(\mathrm{C}_{13}\mathrm{H}_9)_{10}]^{2-}$: The First Molecular Compound with an Icosahedral Ga_{12} Framework[**]

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Starting from metastable AlX and GaX solutions (X = Cl, Br, I), which can be prepared by using a cocondensation method,[1] metalloid clusters such as $\mathrm{Al}_7\mathrm{R}_6^{\,-}$,[2] $\mathrm{Al}_{12}\mathrm{R}_8^{\,-}$,[3] $\mathrm{Al}_{77}\mathrm{R}_{20}^{\,2-}$,[4] ($\mathrm{R}=\mathrm{N(SiMe_3)_2}$) and $\mathrm{Ga}_{22}\mathrm{R}_8$[5] ($\mathrm{R}=\mathrm{Si(SiMe_3)_3}$, $\mathrm{Ge(SiMe_3)_3}$) have recently been synthesized in metathesis reactions. In contrast, there are only a few examples in which polyhedral species such as $(\mathrm{AlR})_n^{\,x-}/(\mathrm{GaR})_n^{\,x-}$ ($x=0$, 1, 2) have been prepared from AlX/GaX solutions or similar routes. In addition to tetrahedral $(\mathrm{MR})_4$ compounds, for example $\mathrm{B}_4\mathrm{R}_4$,[6] $\mathrm{Al}_4\mathrm{Cp}^*_4$,[7] and $\mathrm{Ga}_4[\mathrm{C(SiMe_3)_3}]_4$,[8] as icosahedral species for the two lightest elements of Group 13, besides numerous boron compounds, only the following aluminum species have been structurally characterized: $\mathrm{Al}_{12}i\mathrm{Bu}_{12}^{\,2-}$[9] and $\mathrm{Al}_{12}(\mathrm{AlBr}_{10})\cdot 2\,\mathrm{THF}$.[10, 11] A corresponding molecular gallium compound is as yet unknown,[12] although there are numerous examples of icosahedral partial structures for gallium in solid-state chemistry.[13] We report here on the first molecular compound with an icosahedral Ga_{12} unit.

A metastable GaBr solution, which was obtained by the simultaneous condensation of the high-temperature molecule GaBr with a toluene/THF mixture, was treated with a fluorenyllithium/toluene solution at −78 °C. Allowing the mixture to warm to room temperature, followed by removal of the solvent in vacuo gave a dark red oil, which was subsequently dissolved in THF. Crystals of $[\mathrm{Li(thf)}_4]_2[\mathrm{Ga}_{12}(\mathrm{C}_{13}\mathrm{H}_9)_{10}]$ (**1**) were obtained from the resulting dark red THF solution. The result of an X-ray crystal structure analysis of the anionic Ga_{12} unit is shown in Figure 1.

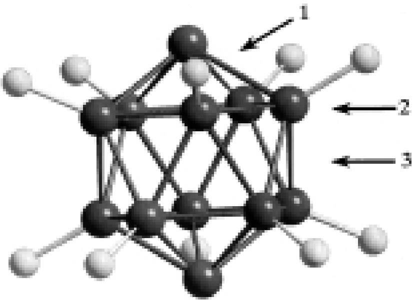

Figure 1. Molecular structure of $\mathrm{Ga}_{12}(\mathrm{C}_{13}\mathrm{H}_9)_{10}^{\,2-}$ in **1**: For clarity only the carbon atom directly bound to the gallium atom is shown in each case for the fluorenyl ligands. Bond lengths (min./av/max.) [pm] in the different regions labeled by numbered arrows: $d(\mathrm{Ga{-}Ga})_1=264.72(7)/265.3/265.87(7)$, $d(\mathrm{Ga{-}Ga})_2=258.27(7)/258.9/259.14(6)$, $d(\mathrm{Ga{-}Ga})_3=267.33(9)/268.4/269.69(8)$.

The structure reveals that fluorenyl ligands are only bound to ten of the twelve gallium atoms, which are arranged in the form of an icosahedron. This iscosahedron is slightly elongated in the direction of the “naked” gallium atoms, thus the longest Ga–Ga contacts (268.4 pm) are found between the two Ga_5 rings. The distances between the “naked” Ga atoms and the Ga atoms of the respective Ga_5 rings (265.3 pm) are only slightly shorter. The shortest Ga–Ga distances (258.9 pm) of the Ga_{12} framework are found in the Ga_5 rings. The ten fluorenyl ligands are each bound to one gallium atom (205.9 pm) in a σ-like fashion and are tilted in a regular fashion in one direction, which is particularly evident on inspection of **1** along an axis running through the two “naked” Ga atoms (Figure 2).

Since the question of whether the “naked” Ga atoms are each saturated by a H atom could not be answered unambiguously from the X-ray structure analysis, we recorded IR spectra on the crystals; however, these revealed no indications of a Ga–H bond. These experimental findings were confirmed by quantum-chemical calculations,[14] which showed that the Ga–Ga and Ga–C distances calculated for the model compound $\mathrm{Ga}_{12}(\mathrm{CH}_3)_{10}^{\,2-}$ are in good agreement with those measured in **1**.[12]

In order to compare the bonding in **1** with the Wade-like bonding in polyhedral boranes by using simple MO diagrams, we performed additional density functional theory (DFT) calculations for $\mathrm{Ga}_{12}\mathrm{H}_{12}^{\,2-}$ (**1a**), $\mathrm{Ga}_{12}\mathrm{H}_{10}^{\,2-}$ (**1b**), $\mathrm{B}_{12}\mathrm{H}_{12}^{\,2-}$ (**1a′**),

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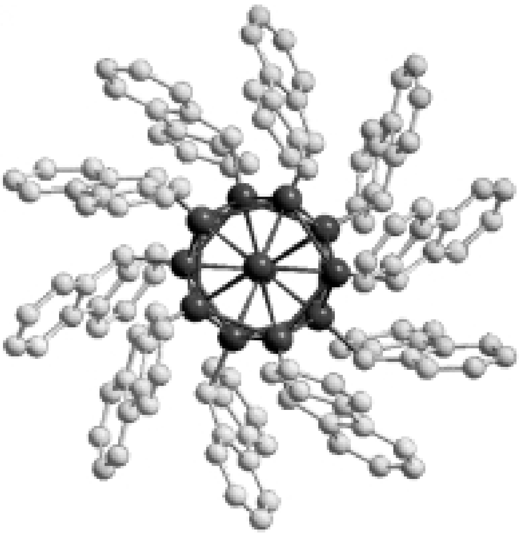

Figure 2. Molecular structure (hydrogen atoms omitted) of $Ga_{12}(C_{13}H_9)_{10}^{2-}$ in **1**. View along one the axes running through the two "naked" Ga atoms.

and $B_{12}H_{10}^{2-}$ (**1b′**). These revealed that the M_{12}^{2-} frameworks in **1a** and **1a′** are held together by 26 electrons and those in **1b** and **1b′** by 28 electrons. The principle difference between the boron and gallium species is that in the boron clusters four (**1a′**) and five MOs (**1b′**), respectively, lie above the MOs for the B–H bonds, whereas the number of framework MOs lying above the Ga–H bonding MOs for the corresponding gallium compounds are eight (**1a**) and nine (**1b**), respectively. This means that the framework MOs found in the gallium compounds are more diffuse, which is a clear indication of the greater "metalliod" character of the gallium compounds (see below) and their expected spontaneous decomposition with metal deposition.[15] The preference of a $Ga_{12}R_{10}^{2-}$ species over a hypothetical $B_{12}H_{10}^{2-}$ species (each in D_{5d} symmetry) is likewise clearly evident from DFT calculations: The HOMO (a_{2u}) in $B_{12}H_{10}^{2-}$ is destabilized by about 3.8 eV compared to the next lower lying MO (e_{2u}), whereas the HOMO (e_{2u}) for $Ga_{12}H_{10}^{2-}$ is only about 0.1 eV above the MO (e_{1u}) lying directly below it. This means that a hypothetical icosahedral $B_{12}H_{10}^{2-}$ species with the 28 framework electrons necessary for a *nido* framework and an energetically high-lying HOMO (see above) should be stabilized by oxidation or reduction of the symmetry in the boron framework. In contrast, the observation of the distorted icosahedral $Ga_{12}R_{10}^{2-}$ ion in **1** is strong evidence for the different bonding in such Ga_n polyhdera. Similar bonding to that in **1** might be present in $Al_{12}(AlBr_2)_{10}$ (**2**), which we prepared recently, although in **2** a distortion different to that in **1** is observed in the Al_{12} icosahedron ($d(Al{-}Al)_1 = 265.0$, $d(Al{-}Al)_2 = 276.7$, $d(Al{-}Al)_3 = 269.2$ pm; numbering as in Figure 1). The $Al_{12}iBu_{12}^{2-}$ icosahedron **3**[9] is a "true" *closo* cluster as defined by Wade, since here all the distances are almost the same (267.9–269.6 pm). As expected the average Ga–Ga distances in **1** are significantly shorter than the Al–Al distances in **3**, since Ga_2R_4 species also display a shortening of about 3% of these distances over those in Al_2R_4 compounds.[16]

The results presented here show that in contrast to the Wade-like bonding system of **3**, a different description of the bonding is necessary for **1**. An interpretation which appears to us to be plausible is briefly presented as follows: In a hypothetical cleavage of two R^- groups from $Ga_{12}R_{10}^{2-}$, a neutral $Ga_{12}R_8$ compound would be formed with the same average oxidation state of the Ga atoms as in **1**. Thus, the relationship to the recently published metalloid clusters $In_{12}R_8$[17] and $Al_{12}R_8^-$ [3] is clearly apparent. Whereas the latter two compounds are intermediates with "metallic" partial structures on the route to the metal, an icosahedral structure is observed for **1**, however, with an electronic structure unexpected for polyhedra (see above). This finding is nevertheless plausible because gallium, in contrast to the more typical metals Al and In, contains icosahedral units in the δ-modification of the element.[18] Thus, the formation of element-like, metalloid structures appears in the cases considered here ($Ga_{12}R_{10}^{2-}$, $In_{12}R_8$, $Al_{12}R_8^-$) to be the main driving force in the disproportionation. This conclusion, however, does not mean that Wade-like species do not form in such reactions as precursors, which, however, have only been isolated in a few cases to date (e.g. $Al_{12}iBu_{12}^{2-}$ [9]).

Experimental Section

Fluorenyllithium (225 mg, 1.33 mmol) was placed in toluene (15 mL) and cooled to −78 °C. GaBr solution (4.2 mL; 1.25 mmol of a 0.3 M solution in toluene/THF (3/1)) was added slowly to this suspension at −78 °C by using a steel cannula. The solution was subsequently allowed to warm to room temperature slowly with stirring. This gave a pale red solution and a black residue. After removal of the solvent in vacuo, a black residue remained, which was washed with pentane and toluene and then taken up in THF. This gave a dark red extract and a yellow-orange residue. The residue was identified by qualitative methods as LiBr. The product **1** was obtained in crystalline form from the THF extract by layering the solution with heptane. Yield: 40 mg of dark red crystals, 0.013 mmol, 12.5%.

Since the resulting crystals could not be redissolved either in benzene or in THF, no NMR data have been obtained to date. The IR spectrum (KBr disk) shows no other absorption bands apart from those for the fluorenyl ligand.

Crystal structure data of **1**: $[Li(thf)_4]_2[Ga_{12}(C_{130}H_{90})]$, $M_r = 3077.99$, crystal dimensions $0.2 \times 0.2 \times 0.3$ mm, triclinic, space group $P\bar{1}$, $a = 17.565(2)$, $b = 17.694(2)$, $c = 17.737(2)$ Å, $\alpha = 63.45(1)$, $\beta = 85.54(1)$, $\gamma = 62.71(1)^\circ$, $V = 4325.8(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.379\ g\,cm^{-3}$, $\mu_{Mo} = 1.8976\ mm^{-1}$, $2\theta_{max} = 51.74^\circ$, 33554 measured reflections, 15572 independent reflections ($R(int.) = 0.0416$), absorption correction: numerical (min./max. transmission 0.527/0.709), $R_1 = 0.0453$, $wR_2 = 0.1208$. Stoe IPDS diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 200 K). The structure of **1** was solved by direct methods and refined against F^2 for all observed reflections. Programs applied: Shelxs and Shelxtl (G. M. Sheldrick, Universität Göttingen). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138288. 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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Novel Oxyfunctionalized Phosphonite Ligands for the Hydroformylation of Isomeric *n*-Olefins

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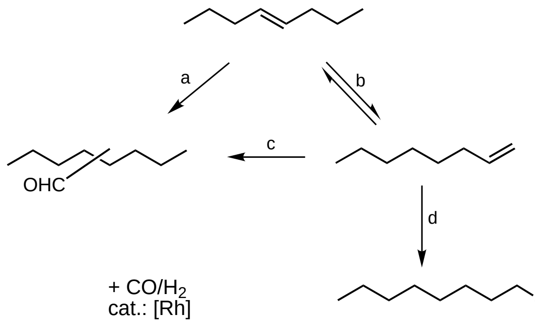
Hydroformylation (oxo synthesis) is one of the most important industrial procedures carried out under homogeneous catalysis. The high economic significance of this C–C coupling reaction results from the successful production of over six million tonnes per year of aldehydes and subsequent products for the plasticizer industry, with propylene as the most important reagent.[1] Knowledge gained from experience demonstrates the advantages of ester plasticizers with a low degree of branching and C-numbers from nine upwards for the alcohol components. An olefin raw material for this application is a technical octene mixture, for which complete conversion of all isomers present and control of regioselectivity to the benefit of terminal aldehyde products are of equal importance (Scheme 1). Hitherto, these two parameters could only be fulfilled by cobalt catalysis under severe reaction conditions. Characteristic productivities are 0.1–0.4 $t\,m^{-3}h^{-1}$ and selectivities for the terminal aldehyde of 50–85%, which are achieved with 0.1–1% Co at pressures of 80–350 bar and temperatures of 160–190°C, as well as an undesirable and extensive hydrogenation activity.[1]



Scheme 1. Isomerizing hydroformylation of internal olefins with the example of 4-octene. a) hydroformylation, b) isomerization, c), d) hydroformylation.

The elimination of these disadvantages by, for example, the use of novel metal complexes, ligands, and technologies is one of the current demands placed upon this area. Highly selective rhodium catalysts based upon bidentate aryl phosphites and diphosphanes with a large coordination angle already exist for the conversion of terminal, long-chain olefins.[2] However, where internal olefins are concerned, technically useful activity is exhibited only with short-chain homologues such as 2-butene.[1,3] Thermally more stable diphosphanes with rigid, bidentate structure and a bias towards *trans* coordination give *n*-selectivities of up to 86% *n*-nonanal from *trans*-octene-4 at very low turnover frequencies of 15 h^{-1}.[4] In the case of terminal olefins the regioselectivity targeted through the use of diphosphanes of selected structure under the assumption of irreversible olefin insertion may also be reasoned on theoretical grounds.[5] On the other hand, structure prediction for ligands which induce *n*-selectivity and, within the context of target position, necessarily also olefin isomerization is still nonexistent.

Esters of phosphonous acids have hitherto found little application as ligands in homogeneous catalysis.[6] There are examples of oxo reactions with the highly reactive propylene as reagent.[6c] Here we demonstrate that compounds of this class are highly suitable for the hydroformylation of long-chain olefins.

For our investigations we chose the readily available and conformationally flexible phosphonites **4a–d** and **5**, which in each case contain a second donor function in the 2′-position.

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