A Ga_8R_6 Cluster as an Ideal Model for a Metal–Metal Bond?[**]

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*Dedicated to Professor Kurt Dehnicke
on the occasion of his 70th birthday*

In the 1960s the primary interest in simple cluster compounds such as $[(CO)_3CpW{-}WCp(CO)_3]$, $[(CO)_5Mn{-}Mn(CO)_5]$, and ClHg–HgCl lay in the bond between the metal atoms, since here the complex bonding situation in metals is reduced to a two-electron–two-center (2e2c) bond.[1] Since the ligands, such as halogen atoms or CO, undergo strong interactions with the metal atoms and thus strongly influence the bond between the two metal atoms, such a bonding situation is fundamentally different from that in metals.

Therefore compounds of the type $Y_3X{-}XY_3$ (X, Y = metal atoms, that is two linked Y_3X tetrahedra) with bonding interactions between the Y atoms are of particular significance. However, there are to date only a few examples in which some of the metal atoms are replaced by nonmetal atoms: X = C, Y = Co,[2] Y = Fe;[3] X = N, Y = Au;[4] X = Hg, Y = Pt,[5] and X = (As,Co), Y = Co.[6] The only species known to us which approaches the desired model compound is $[Ir_8(CO)_{22}]^{2-}$,[7] in which a Ir_2 unit is bound on both sides to an Ir_3CO_{11} group, and some of the CO ligands function as bridging ligands. Thus to date there is no simple model compound for a typical metal–metal bond as defined by the above-mentioned limitations, in which eight identical metal atoms, in the form of two linked M_4 tetrahedra, form 13 metal–metal bonds ($2 \times 6 + 1$), but only six metal–ligand bonds.

Recently, however, we have achieved a first step in this direction through the synthesis of an Al_7R_6 cluster,[8] in which two Al_4 tetrahedra are linked through a "naked" Al atom, such that 12 metal–metal contacts are present together with six metal–ligand bonds. Herein we present the first molecular example for an ideal metal–metal bond as defined by the above-mentioned criteria, in which in a Ga_8R_6 unit two Ga_4 tetrahedra are linked through a common "naked" Ga atom. $C(SiMe_3)_3$ (trisyl) groups were used as ligands, with which both the first Ga_4R_4 cluster[9] and recently a Ga_{19} species were obtained.[10]

Reaction of trisyllithium dissolved in toluene at −78 °C with a solution of Ga^IBr in toluene/THF (obtained by cocondensation of the high-temperature molecule GaBr) resulted in a solution that was stable at room temperature. After removal of the solvent, a black residue remained. Extraction with pentane and subsequently with toluene gave black filtrates in each case; a Ga-centered Ga_{19} cluster was crystallized from the toluene solution,[10] and we have now also obtained black crystals in the form of hexagonal platelets from the pentane extract. The results of the X-ray structure analysis show that these crystals are the neutral octagallane $[Ga_8\{C(SiMe_3)_3\}_6]$ (**1**) (Figure 1).

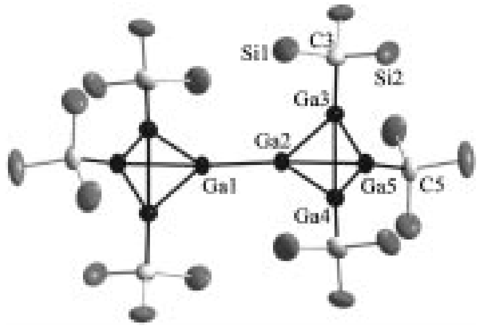

Figure 1. Molecular structure of **1** (without methyl groups; thermal ellipsoids 50%). Selected bond lengths [pm] and angles [°]: Ga1-Ga2 261.43(11), Ga2-Ga3 260.54(8), Ga2-Ga4 260.54(8), Ga2-Ga5 264.03(11), Ga3-Ga4 264.81(9), Ga3-Ga5 263.65(8), Ga3-C3 204.8(4), Ga5-C5 204.3(5); Ga1-Ga2-Ga3 142.97(2), Ga1-Ga2-Ga5 147.11(4), Ga3-Ga2-Ga4 61.09(3), Ga2-Ga4-Ga5: 60.49(3), Ga2-Ga4-Ga3 59.455(13), C5-Ga5-Ga2 143.61(16), C3-Ga3-Ga4 146.75.

The Ga–Ga distances in **1** vary within a narrow range (260.5–264.8 pm), and consequently the angles within the triangular faces of the tetraheda deviate by a maximum of 1° from the ideal value of 60°. The ligands are bound to the gallium atoms with an average Ga–C distance of 204.5 pm. The Ga–Ga as well as the Ga–C bonds in **1** are significantly shorter than those in the tetrahedral complex $[Ga_4\{C(SiMe_3)_3\}_4]$ ($d(Ga{-}Ga) = 268.3$, $d(Ga{-}C) = 207.4$ pm (av)). This finding shows that the $C(SiMe_3)_3$ ligand has a large steric demand and thus in situations in which steric overloading occurs such as in Ga_4R_4 compounds leads to increased bond lengths in the Ga_4 framework and in the Ga–R bonds.

Since as outlined in the introduction the structural element depicted in Figure 1 of two tetrahedral M_4R_3 units linked by a metal–metal bond is hitherto unknown for clusters containing one element, we have examined this archetype of a metal–metal bond in more detail by carrying out density functional theory (DFT) calculations[11] on the model compound Ga_8H_6 (**1a**). The results of these calculations are given in Table 1 and are compared to the analogous results for Ga_2H_4 (**1b**) and Ga_4H_4 (**1c**).

As expected the charges of the Ga atoms in the listed compounds differ only slightly. The central Ga atoms in **1a** bear a slightly negative partial charge (in contrast to the positive partial charges, for example, in localized metal–metal bonds mentioned in the introduction such as in ClHg–HgCl), so that these species contain metal–metal interactions that are close to metallic metal–metal bonds, which for the first time allows a comparison of an extensively localized bond in a molecular unit with the delocalized bonding in metals. However, the distances found for **1** differ from the ones calculated for **1a** with regard to absolute values

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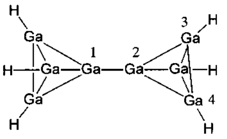
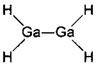
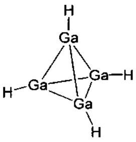
Table 1. Ga–Ga distances d(Ga–Ga), force constants f, charges q, and ^{71}Ga NMR shifts δ of the calculated model compounds **1a**–**1c**.

Compound	 Ga_8H_6 **1a**	 Ga_2H_4 **1b**	 Ga_4H_4 **1c**
d(Ga–Ga) [pm]	253.8 (Ga1–Ga2) 259.4 (Ga2–Ga3) 255.8 (Ga3–Ga4)	246.2	256.7
f [mdyn Å^{-1}]	0.8 (Ga1–Ga2)	1.1	0.6
q	−0.1 (Ga1) 0.0 (Ga3)	0.1	0.0
δ(^{71}Ga)	1028 (Ga1) 942 (Ga3)	705	986

and their progression. This finding is plausible since the sterically highly demanding $C(SiMe_3)_3$ group leads to very long Ga–Ga bonds such as found in the Ga_4R_4 compound.[9] This bulkiness of the ligand framework also results in an increase of the central Ga–Ga distance in **1**, as can be clearly seen in the space-filling model (Figure 2).

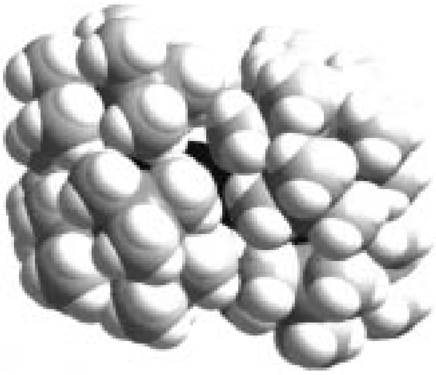


Figure 2. Space-filling model of **1**.

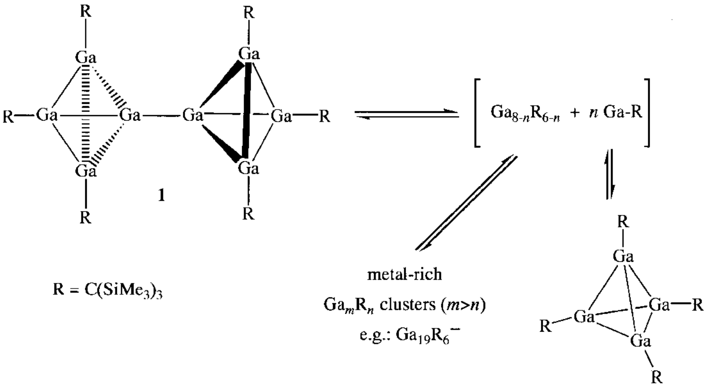
Without these repulsive interactions the central Ga–Ga bond, as the calculations show, should be significantly shorter than the other Ga–Ga bonds, since the central Ga_2 unit is mainly based on 2e2c-σ bonding (HOMO, a_{1g}), whereas the six remaining Ga–Ga bonds in the $(RGa)_3Ga$ units are based on four delocalized molecular orbitals (a_{1g}, t_{2u}).

Parallel to the Ga–Ga distances, the corresponding Ga–Ga force constants also change, that is the Ga–Ga bond of Ga_2H_4 is significantly stronger (1.1 mdyn Å^{-1})[12] than the one of the central Ga_2 unit in **1**. In contrast, the latter is slightly larger than the one of the Ga_4H_4 tetrahedron **1c**. Evidently, the strong delocalization of the electrons within the two Ga_4 fragments leads to this destabilization of the linking Ga–Ga bond in **1**. This bond lengthening should be even larger on increasing the coordination numbers at the central Ga atoms, for example, the linkage of two octahedral or icosahedral Ga_n polyhedra through common Ga–Ga bonds.

The electronic relationship of **1** to a corresponding Ga_4R_4 unit is already clear through the differing color (**1** is black, Ga_4R_4 in contrast red). This finding is in agreement with the results of DFT calculations, according to which significantly different HOMO–LUMO distances were calculated for **1a** and Ga_4H_4: 1.27 and 2.46 eV, respectively.

The calculated ^{71}Ga shifts for **1a** and **1c** must be considered together with the experimental and theoretical results for a Ga_{19} cluster ($[GaGa_{12}(GaR)_6]^-$; R = $C(SiMe_3)_3$):[10] In this case calculations show that the signals of the naked Ga atoms ($GaGa_{12}$) are considerably low-field shifted in comparison to those of the six ligand-bearing Ga atoms; note also that the nature of the ligands strongly influences the shift of the "naked" atoms. Their resonance shifts to higher fields on going from H through CH_3 to $C(SiMe_3)_3$ as ligand. The signals shifted to highest field were found in the ligand-free Ga cluster Ga_{13}^-. Thus the as yet not observed shift of the central Ga atoms in **1** will probably lie significantly shifted to high field in comparison to those calculated in **1a**, whereas the shift of the ligand-bearing Ga atoms will probably be only slightly influenced. Shifts to high field of "naked" Ga atoms, which could for the first time be experimentally confirmed for the Ga_{19} cluster, thus seem to be typical for "metallically" bound metal atoms. The slight shift to high field of the central Ga atoms in **1a** in comparison to the shift in **1c** shows, however, that the electronic environment of the central Ga_2 unit in **1a** is very similar to that in the tetrahedral **1c**. A change of the situation with signals further shifted to high field is only expected for the central Ga_2 unit when the coordination numbers for these atoms increase, that is, when, for example, two icosahedral clusters are linked through a Ga–Ga bond. Such compounds would then be even better model compounds for an isolated metal–metal bond.

In addition to the described special characteristics with regard to structure and bond theory, the formation of **1** also gives an indication of the reactions occurring in solution. For instance, **1**, as a key compound in the construction of larger clusters, could be in equilibrium with other metal-rich species and GaR oligomers (Scheme 1).



Scheme 1. Postulated mechanism of the formation of the metalloid Ga_{19} cluster from **1**.

Compound **1** is the first model compound for a metal atom contact[13] in the form of a nano-metal wire. In this context the results presented here should provide the stimulus or be the gauge for future theoretical and experimental investigations on the reaction between metal atom clusters from their primary contact to their fusion to give larger clusters.

Experimental Section

In a 250-mL bulb $LiC(SiMe_3)_3$ (1.5 g, 6.3 mmol) was placed in toluene (25 mL). After the solution had been cooled to −78°C, GaBr (15 mL of a 0.3 M solution in toluene/THF (3/1), 5 mmol) was added. The reaction mixture was slowly allowed to warm to room temperature, during which the solution became dark red to black. The solvent was then removed in vacuum. The black residue was extracted with pentane. A few black crystals of **1** in the form of hexagonal platelets precipitated from the dark brown pentane extract.

Crystal structure data of **1**: $Ga_8(C(SiMe_3)_3)_6$, $M_r = 1891.3$, crystal dimensions $0.3 \times 0.6 \times 0.6$ mm, monoclinic *c*, space group $C2/m$, $a = 13.203(3)$, $b = 24.704(5)$, $c = 17.382(4)$ Å, $\beta = 103.86(3)°$, $V = 5504.3(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.175$ g cm^{-3}, $\mu_{Mo} = 2.150$ mm^{-1}, $2\theta_{max} = 51.74°$, 16186 measured reflections, 5446 independent reflections ($R_{int} = 0.0841$), absorption correction: numerical (min./max. transmission 0.1630/0.4012), $R_1 = 0.0466$, $wR_2 = 0.1388$. 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 used: 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-151247. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Haag – Dessau Catalysts for Ring Opening of Cycloalkanes

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With the advent of the Auto Oil Programme of the European Union, the aromatics content of gasoline has to be reduced from 45 vol% in 1999 to 42 and 35 vol% in 2000 and 2005, respectively.[1] Therefore, western Europe will probably face a surplus of aromatics, especially toluene, soon. One of the major sources of aromatics is pyrolysis gasoline, a by-product from steamcracking of naphtha for the production of ethene and propene. Given the large growth rate of demand for ethene[2] and propene[3] that is generally forecasted, the production of pyrolysis gasoline—and, hence, of aromatics—will necessarily increase as well. For the conversion of aromatics into a premium synthetic steamcracker feedstock (consisting mainly of ethane, propane, and *n*-butane), two process variants have recently been introduced. In variant 1, the aromatics are directly converted with hydrogen on a bifunctional zeolite catalyst;[4] in variant 2, cycloalkanes, which can easily be obtained from aromatics by state-of-the-art hydrogenation processes, are hydroconverted on acidic zeolite catalysts.[5] In both cases, pyrolysis gasoline is ultimately recycled into the steamcracker and thus removed from the market.

Recently, we observed that the selectivity to *n*-alkanes with two and more carbon atoms (C_{2+}-*n*-alkanes) is very high during the conversion of methylcyclohexane on catalysts that contain noble metals in such small amounts that they can be classified neither as typically bifunctional nor as monofunctional. We report here on these results and their mechanistic implications.

To begin with, the salient mechanistic features of catalytic ring opening of cycloalkanes are briefly sketched (Scheme 1): On bifunctional catalysts, methylcyclohexane is dehydrogenated on metallic sites, and the resulting cycloalkenes are protonated to carbenium ions on acidic sites. Usually, skeletal isomerization into highly branched isomers occurs first, whereupon classical β-scission can proceed. Finally, the diene formed is hydrogenated on a metal site (Scheme 1 a, top).[6, 7] On monofunctional acidic catalysts, two different mechanisms can be operative:[8, 9] On the one hand, β-scission of classical carbenium ions is possible, but the latter can now only form through a bimolecular hydride transfer (Scheme 1 a, bottom). On the other hand, methylcyclohexane can be directly protonated forming a nonclassical carbonium ion with a three-center, two-electron bond in the transition state (Haag – Dessau cracking, Scheme 1 b). If ring opening is accompanied by secondary cracking steps, isoalkanes (no

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