resin had hardened completely the remainder of the uninsulated gold microwire was covered with a thin layer of epoxy resin so that only the (111) face was left exposed. This procedure was successful for microcrystals with $d_{eff} = 10-35$ μm. In the case of smaller SCUMEs, for example with a d_{eff} of 5 μm, a slightly different procedure was used to minimize the capacitative current.[13] In this case a 100 μm length of a gold microwire with a diameter of 3 μm was first fixed to the larger 10 μm wire using the gold paint. The small microcrystal was then fixed to the 3 μm wire using the same procedure described above. Slightly different procedures were used to fabricate SCUMEs with exposed (100) faces.

All electrochemical experiments were carried out in a water-jacketed glass cell with the SCUME, a Pt counterelectrode, and a calomel reference electrode containing 0.05 M KCl. The cell was placed in a Faraday cage and coaxial cables were used to connect the electrodes to the potentiostat. Electrolyte solutions were prepared from $HClO_4$ (Aldrich, 99.999 % pure) diluted to 0.01 M in nanopure water. The solution was purged with argon for 10 min and kept under argon during the measurements. The reference electrode was connected to the body of the cell using a Luggin capillary containing the 0.01 M $HClO_4$ solution. Cyclic voltammograms were recorded by using a EG&G 283 potentiostat connected to a PC minicomputer by a GPIB IEEE-488.2 interface. The current-potential data were acquired digitally.

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$Ga_9(CMe_3)_9$, an Important New Building Block in the Structural Chemistry of the Alkylelement(I) Compounds E_nR_n ($E = B-In$)[**]

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Numerous organoelement cluster compounds of the elements boron, aluminum, gallium, and indium have been published in recent literature. Most of them are difficult to prepare and were isolated in only very poor yield. They often contain cluster anions such as $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ or $[Ga_9\{Si(SiMe_3)_3\}_6]^-$.[1] Beside these ionic derivatives a few neutral cluster compounds such as In_8Ar_4 (Ar = 2,6-dimesitylphenyl) or $In_{12}\{Si(CMe_3)_3\}_8$[2] were synthesized in which the number of the cluster atoms exceeds the number of the substituents. To the best of our knowledge there is no systematic approach to the description of their formation and of their fascinating structural chemistry. Element(I) compounds E_nR_n were isolated and structurally characterized before only as monomers ER or as tetrahedral clusters of the type E_4R_4,[3] in which R denotes very bulky substituents. A neopentylgallium(I) compound was reported in literature,[4] however, it was not isolated in a pure form. For many years we have tried to control the size of E^I clusters by the systematic variation of the steric demand of their substituents. Smaller groups should lead to the formation of larger clusters, which are of particular interest owing to their bonding and broad preparative application in secondary reactions. However, the tendency to disproportionate as a consequence of insufficient steric shielding prevented the isolation of such derivatives.

The reaction of *tert*-butyllithium with gallium trihalides affords tri(*tert*-butyl)gallium[5] in a good yield as well as a small quantity of elemental gallium by a redox reaction. By systematically changing the reaction conditions we attempted to stop the partial reduction of trivalent gallium at an intermediate oxidation state. Finally, we obtained a green solution from which black-green crystals of **1** were isolated in 4 % yield after separation of the alkylgallium(III) compound [Eq. (1)]. Owing to the easy availability of compound **1** a complete characterization was possible despite its low yield. The crystal structure determination[6] revealed a tricapped

$$GaCl_3 + 3\,LiCMe_3 \xrightarrow[-LiCl]{} Ga(CMe_3)_3 + \underset{\mathbf{1}}{Ga_9(CMe_3)_9} \qquad (1)$$

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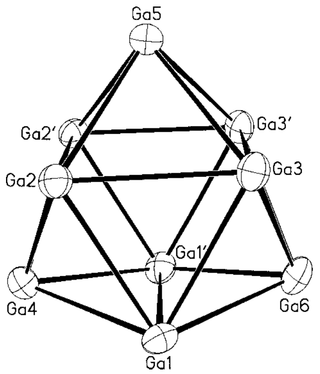

Figure 1. Molecular structure of **1**; the *tert*-butyl groups are omitted for clarity. Only one of the two independent molecules is drawn, the average values are, however, calculated from both independent molecules. Important bond lengths [pm]: Ga–Ga distances to the capping Ga atoms (Ga4, Ga5, Ga6 (Ga7, Ga13, Ga15)): 256.9(1)–261.9(1) (av 258.8); Ga–Ga distances at the edges of the triangle of the prism between the atoms Ga1, Ga2, Ga3 (Ga8, Ga9, Ga13 and Ga10, Ga11, Ga14): 264.06(9)–268.96(9) (av 267.02); Ga1-Ga1′ 300.7(1), Ga2-Ga2′ 304.6(1), Ga3-Ga3′ 291.2(1) [291.39(9)–306.6(1) in the second molecule]; Ga-C 202.5.

trigonal prism of gallium atoms (Figure 1). Three ranges of Ga–Ga bond lengths were observed: short distances of 258.8 pm (av) were detected to the capping Ga atoms, while longer distances of 267.0 pm were found on the triangular faces of the prism. Very long Ga–Ga separations were observed for the edges of the prism perpendicular to these triangles (298.8 pm), which indicate only weak Ga–Ga interactions. Thus, all gallium atoms within the cluster seem to have a connectivity of four. For comparison, the Ga–Ga single bond lengths in tetraalkyldigallium compounds Ga_2R_4 are about 250 pm,[7] while alkyl-substituted tetrahedral tetragallanes Ga_4R_4 have Ga–Ga distances of about 270 pm.[8]

Compound **1** has a surprisingly high thermal stability and decomposes above 228 °C with the formation of elemental gallium. Powdered samples of **1** remained unchanged in air over a period of about 30 min. The UV/Vis spectrum showed two absorptions in the visible region at 480 and 600 nm. In comparison to gallium(III) compounds, the proton resonances of the *tert*-butyl groups in the ^{1}H NMR spectrum are only slightly shifted to a lower field by about 0.3 ppm ($\delta = 1.48$). However, an extreme low-field shift ($\delta < 30$ in compounds possessing trivalent gallium atoms) was observed for the resonances of carbon atoms attached to gallium ($\delta = 100.4$). Tetrahedral E_4R_4 clusters bearing tris(trialkylsilyl)methyl substituents showed a less dramatic shift of $\delta = 60-64$.[8] An absorption at 513 cm^{-1} in the IR spectrum was assigned to the Ga–C stretching vibration. A ^{71}Ga NMR spectrum could not be recorded owing to the quadrupole moment of gallium and the low local symmetry at each gallium atom.

According to cyclic voltammetric investigations the uptake of an electron is electrochemically reversible; it leads in *o*-difluorobenzene or dichloromethane to the corresponding radical anion **2**, accompanied by a lightening of the color of the solution.[9] The radical anion **2** was stable at room temperature and was further reduced at an about 1 V more negative potential in an irreversible two-electron reduction step. Cooling to −78 °C did not lead to an improvement of the reversibility behavior. The oxidation was also completely irreversible in a multielectron process in which the current intensity corresponded approximately to the loss of one electron per gallium atom.

The ESR spectroscopic characterization of the radical **2** was only possible at very low temperature owing to fast relaxation.[9] The reason for this may be the relatively high symmetry of **2**, which leads to energetically similar states and the occupation of neighboring, partially degenerate orbitals by the unpaired electron. Similar observations were reported for the distorted octahedral hexaborates $[B_6X_6]^{\bullet-}$ (X = halogen).[10] Also the splitting of the *g* components of **2** (2.173, 2.06, 1.95) is similar to that of, for example, $[B_6Br_6]^-$ (2.15, 2.09, 1.88).[10] Thus, these data verify a distribution of the unpaired electron over at least large parts of the cluster skeleton. Accordingly, the hyperfine splitting by coupling with the isotopes ^{69}Ga and ^{71}Ga (each $I = 3/2$) was not observed owing to the overlap of the expected large number of lines.

Quantum-chemical calculations of the methyl compound Ga_9Me_9 (**1a**) verified the structural parameters of **1** with three characteristic ranges of Ga–Ga distances and the elongation of the cluster parallel to its threefold rotation axis.[11] For comparison, we also calculated the radical anion **2a** which was reversibly generated by an electrochemical experiment and detected by ESR spectroscopy.[11] Remarkably, the nonagallium cluster showed behavior similar to the corresponding boron compounds $[B_9X_9]^{n-}$ (X = H, halogen; $n = 0,1,2$).[12] The addition of one electron leads to a strengthening of the Ga–Ga interaction parallel to the long edges of the trigonal prism and to a compression of the cluster (Ga–Ga: from 298.2 in **1a** to 281.6 pm in **2a**). The distances to the capping Ga atoms remained almost unchanged (256.3 (**1a**) and 254.4 pm (**2a**)), while the edges of the triangles of the prism became longer (267.3 (**1a**) and 275.1 pm (**2a**)). Thus, an almost undistorted equilateral trigonal prism is present in the radical anion.

For the first time, the influence of the steric demand of the substituents on the size of a third main group cluster was verified by the synthesis of compound **1**. This will stimulate further experiments toward the synthesis of other alkylelement(I) compounds bearing smaller alkyl groups and having novel structures. Furthermore, the synthesis of **1** opens the access to a chemistry similar to that of polyborates. As impressively shown with the related compounds E_4R_4,[3] we expect a broad preparative application of **1**, in particular in those cases in which the high steric shielding of the derivatives previously employed prevented secondary reactions.

Experimental Section

n-Pentane and *n*-hexane were dried over $LiAlH_4$. Freshly sublimed $GaCl_3$ (7.33 g, 0.042 mol) in *n*-hexane (90 mL) was treated with *tert*-butyllithium (78 mL of a 1.6 M solution in *n*-hexane) over a period of 1 h. The mixture was heated under reflux for 16 h, cooled to room temperature, and filtered. The volatile components were removed in vacuum at room temperature. At the same temperature and at a pressure of 10^{-3} Torr tri(*tert*-butyl)gallane was distilled in a trap cooled with liquid nitrogen (yield: 6.83 g, 68 %). The green residue was dissolved in pentane (25 mL) and filtered. The filtrate was evaporated, the residue was thoroughly evacuated and recrystallized from *n*-pentane or diisopropyl ether (yield: 0.19 g, 4 %). Decomposition (under argon, sealed capillary): 228 °C. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.48$; ^{13}C NMR (125.8 MHz, C_6D_6): $\delta = 100.4$ (GaC), 32.2 (CH_3). IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 1465 vs, 1387 w, 1358 vs, 1308 m, 1242 vs ($\delta(CH_3)$); 1188 w, 1158 vs, 1005 m ($\nu_s(C_3C)$); 984 m, 937 m (CH_3 rocking); 805 vs ($\nu_{as}(C_3C)$); 513 m (ν(GaC)); UV/Vis (*n*-hexane): λ_{max} [nm] (lg ε): 245 (4.6), 480 (3.5), 600 (2.9).

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[9] Cyclic voltammogram of **1** in $\mathrm{CH_2Cl_2}$/0.1 M $\mathrm{Bu_4NPF_6}$ or 1,2-difluorobenzene/0.1 M $\mathrm{Bu_4NPF_6}$ at 298 K: Reversible reduction at $E(1/2) = -1.74$ V (vs. $[\mathrm{Fe(C_5H_5)_2}]^+/[\mathrm{Fe(C_5H_5)_2}]^0$); irreversible two-electron reduction at -2.70 V; irreversible multielectron oxidation at 0.40 V ($100\ \mathrm{mV\,s^{-1}}$). ESR spectrum of **2**, generated electrochemically in $\mathrm{CH_2Cl_2}$/0.1 M $\mathrm{Bu_4NPF_6}$ at 298 K, measured in a glassy frozen solution at 3.4 K: $g_1 = 2.173$, $g_2 = 2.06$, $g_3 = 1.95$. Owing to very fast relaxation no signal was observed above 110 K.

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[11] Structural parameters of the model compounds **1a** and **2a** were optimized at the HF/6-31G* level with the program package Gaussian 98. This level has previously been shown to be reliable for gallium compounds. $\mathrm{Ga_9Me_9}$ (**1a**): Ranges of Ga–Ga distances: 255.1–257.6 pm to the capping Ga atoms (av 256.3 pm), 266.6–268.4 pm for the edges of the triangles of the prism (av 267.3 pm), 294.7–303.1 pm for the edges of the prism parallel to the threefold rotation axis (av 298.2 pm); Ga–C 197.7 pm (av). $[\mathrm{Ga_9Me_9}]^-$ **2a**: Ranges of Ga–Ga distances: 253.8–255.1 pm to the capping Ga atoms (av 254.4 pm), 274.7–275.5 pm for the edges of the triangles of the prism (av 275.1 pm), 280.8–282.7 pm for the edges of the prism parallel to the threefold rotation axis (av 281.6 pm); Ga–C 200.3 pm.

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Stereoselective Multiple Functionalization of Pyrylium Salts by Domino Reactions with 2-Silyloxybuta-1,3-dienes**

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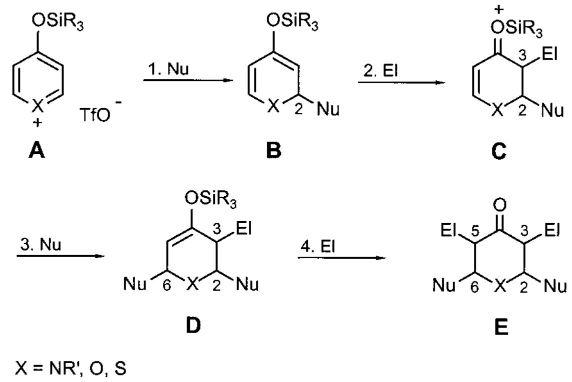
Christopher Lehmann, and Mathias Noltemeyer

The development of multicomponent domino reactions is particularly attractive as these allow the stereoselective conversion of several simple substrates into complex target molecules, such as annulated or bridged polycycles, in a single step.[1] Pyrylium salts are easily accessible, reactive heteroarenes that react preferably with nucleophiles. Apart from transformations that proceed with conservation of the pyran ring, we are also familiar with reactions in which the primary adducts are stabilized by ring opening or subsequent ring transformation.[2] In contrast, only a few stereoselective reactions that start from pyrylium salts are known to result in complex ring systems. One exception is the 1,3-dipolar cycloadditions of 3-oxidopyrylium salts, which have initially been developed by Sammes et al. and later by Wender, Mascareñas, and Magnus and co-workers to provide an attractive route to various ring systems and natural products.[3]

One concept that may be applied to yield products of a higher complexity in diastereomerically pure form from simple components is the multiple functionalization of positively charged heteroarenes. Here, **A** first reacts regioselectively with a nucleophile at C-2. The resulting enol ether **B** can then react with an electrophile at C-3 forming the Michael acceptor **C**. Subsequent transformation with a nucleophile at C-6 and an electrophile at C-5 yield the trisubstituted **D** and the tetrasubstituted heterocycle **E**, respectively (Scheme 1). Following research on the selective mono- and bisfunctional-



Scheme 1. Multiple functionalization of positively charged heteroarenes.

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