Multiple Ga–Ga Bonding Character in $Na_2[Ga(GaTrip_2)_3]$, and a Comparison with Neutral $Ga(GaTrip_2)_3$ (Trip = 2,4,6-$i$$Pr_3C_6H_2$)[**]

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The syntheses and structures of the neutral digallane(4) **1** (Ga–Ga = 2.515(3) Å; Trip = 2,4,6-$i$$Pr_3C_6H_2$) and its singly reduced salt **2** (Ga–Ga = 2.343(2) Å) were reported in 1993.[1] The structural and spectroscopic data for the latter were consistent with the formation of a Ga–Ga π bond of formal order 0.5 as a result of the reduction.

$Trip_2GaGaTrip_2$ **1**

$[Li([12]crown\text{-}4)_2][Trip_2GaGaTrip_2]$ **2**

In effect, the added electron occupies a π-molecular orbital formed by overlap of a p orbital from each gallium atom. The attempted further reduction of **2** in diethyl ether to give the doubly reduced ion $[Trip_2GaGaTrip_2]^{2-}$, which should have a formal Ga–Ga π bond order of 1, was unsuccessful owing to apparent decomposition of the dianionic species.[1a] Detailed investigations by Uhl and co-workers[2] have shown that further reduction of the related radical anion species $[R_2AlAlR_2]^-$ (R = $CH(SiMe_3)_2$) in 1,2-dimethoxyethane leads to the formation of ether cleavage products with no Al–Al bonds. In view of the apparent reactivity of the aluminum and gallium dianions toward ethers, it was decided to attempt a double reduction of **1** by using a less reactive solvent such as triethylamine in order to synthesize a doubly reduced, multiply bonded species. We now report some findings of these investigations, which have resulted in the isolation of the novel dianion **3** and its neutral analogue **4**.

$Na_2[Ga(GaTrip_2)_3]$ **3**

$Ga(GaTrip_2)_3$ **4**

The dark red dianion **3** was synthesized by the treatment of **1** in triethylamine with a tenfold excess of sodium for about three days at room temperature. Large black crystals, suitable for X-ray crystallography, which correspond to the formula $\mathbf{3}\cdot 3C_6H_6$ were grown from solutions in benzene. The X-ray crystal structure analysis[3] showed that molecules of **3** were composed of a central gallium atom (Ga(1)) bound to three $GaTrip_2$ moieties. The structure (Figure 1) is completed by two sodium ions which are sandwiched by Trip groups. Both Trip substituents attached to Ga(2) and one Trip substituent from Ga(3) and Ga(4) are involved in the complexation of the Na^+ ions. The coordination at all four gallium atoms is planar but there are significant distortions from idealized 120° angles. For example, at the central gallium atom, the Ga(3)-Ga(1)-Ga(4) angle of 107.66(4)° is at least 15° narrower than the other two angles. Furthermore, at the peripheral gallium atoms the C-Ga-C angle is always narrowest, whereas at Ga(3) and Ga(4), the Ga(1)–Ga(3/4)-C(*ipso*) angle involving rings complexed to the Na^+ ions are 9 to 13° narrower than the Ga(1)-Ga(3/4)-C(*ipso*) angle involving uncomplexed rings. The Ga(1)–Ga(2) bond (2.364(1) Å) is about 0.04 Å shorter than the Ga(1)–Ga(3) (2.406(1) Å) or the Ga(1)–Ga(4) (2.398(1) Å) bonds. The shorter Ga(1)–Ga(2) distance corresponds to a lower torsion angle (17.7°) between the coordination planes at Ga(1) and Ga(2) than between the coordination planes Ga(1) and Ga(3) and Ga(1) and Ga(4) (angles 32.2° and 28.5°, respectively).

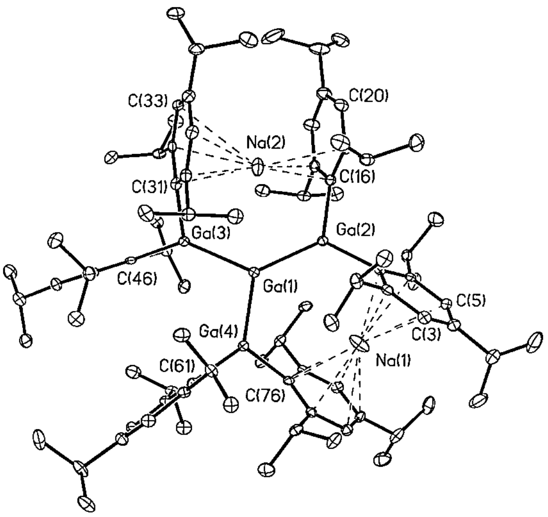

Figure 1. Molecular structure of **3** in the crystal (H atoms omitted). Selected bond lengths [Å] and angles [°]: Ga(1)–Ga(2) 2.3641(10), Ga(1)–Ga(3) 2.4062(10), Ga(1)–Ga(4) 2.3981(10), Ga(2)–C(1) 2.044(5), Ga(2)–C(16) 2.051(5), Ga(3)–C(31) 2.060(5), Ga(3)–C(46) 2.023(5), Ga(4)–C(61) 2.019(5), Ga(4)–C(76) 2.058(5); Ga(2)-Ga(1)-Ga(3) 128.96(3), Ga(2)-Ga(1)-Ga(4) 123.18(4), Ga(3)-Ga(1)-Ga(4) 107.66(4).

In spite of these distortions, which are attributable either to steric congestion or Na^+ ion complexation, the structural parameters are consistent with the formation of a two-electron π bond which is essentially delocalized over the Ga_4 array to afford a species with a formal Ga–Ga bond order of 1.33.[4] The average Ga–Ga distance in **3** (2.389(17) Å) is longer than that in the radical anion $[Trip_2GaGaTrip_2]^-$ (2.343(2) Å; formal Ga–Ga bond order = 1.5)[1a] but is shorter than those in the cyclic compounds $M_2[Ga(2,6\text{-}Mes_2C_6H_3)]_3$ (ca. 2.44 Å; formal Ga–Ga bond order = 1.33; M = Na or K; Mes = mesityl).[5] An additional feature of the structure of **3** is that all the Trip rings complexed to the Na^+ ions are bent towards the ion (Figure 1). The bending, which can be quantified by the deviation of the Ga–C(*ipso*) bonds from the planes of the aromatic rings, ranges between 9.6 and 14.3°, whereas for the two noncomplexed rings the deviation is only 2.4 and 3.4°. The apparently tight complexation of the Na^+ ions is consistent with the structural distortions described above. Moreover, the greater Ga(1)–Ga(2) bond shortening is in keeping with recent calculations on reduced organogallium complexes which suggest that Na^+ ion complexation can effect a significant contraction of Ga–Ga bond length.[6] However, the Na^+ ions are not bound equally strongly to the carbon atoms of the Trip rings (Na–C = 2.548(5) – 2.824(6) Å; Na – centroid 2.464 – 2.771 Å) but interact most strongly with

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the *ipso* carbon atoms. Also, the Na^+ ions deviate by 0.25 Å (Na(1)) and 0.55 Å (Na(2)) above and below the Ga_4 plane.

The neutral compound **4** was obtained as orange crystals by the reaction of **3** with one equivalent of dry O_2. The X-ray crystal structure analysis of **4** (Figure 2) shows that there are two half molecules per asymmetric unit each of which has a crystallographically required twofold axis of symmetry along one of the Ga–Ga bonds. Essentially, the structure of **4** has a similar arrangement to **3** but without the presence of the Na^+ ions. The most interesting difference between **3** and **4** is that the Ga–Ga bonds are significantly lengthened (by ca. 0.08 Å) to an average value of 2.476(7) Å. This lengthening is consistent with a reduction of the overall gallium bond order to unity. This Ga–Ga distance is well within the known range for single bonds between three-coordinate gallium moieties.[7] Moreover, it is slightly shorter than that in **1** (2.515(3) Å). This is in agreement with the recently reported structure of $In(InTrip_2)_3$ which also has shorter In–In bonds (2.696(2) Å) than those in $Trip_2InInTrip_2$ (2.775(2) Å).[8] Another notable feature of the structure of **4** is that the torsion angles between the coordination planes at the peripheral gallium atoms Ga(2) and Ga(3) are increased to 81.4° and 72.9° which is consistent with the elimination of Ga–Ga π bonding in **4**. The lengthened Ga–Ga bonds make for a more sterically relaxed structure and this is reflected in the fact that the average C-Ga-C angle in **4** is significantly wider than that in **3**.

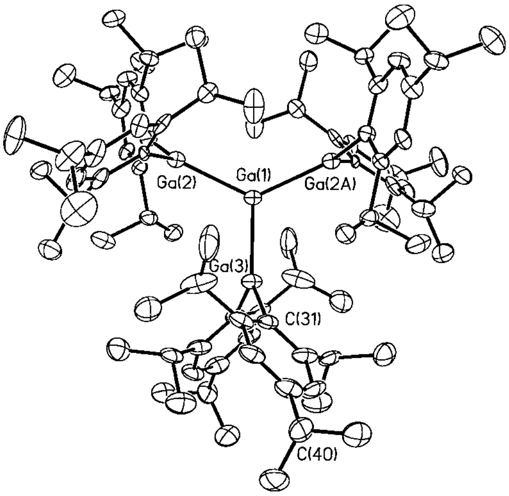

Figure 2. Molecular structure of one of the two molecules of **4** in the crystal (H atoms omitted). Selected bond lengths [Å] and angles [°] from both molecules: Ga(1)–Ga(2) 2.4813(17), Ga(1)–Ga(3) 2.465(3), Ga(2)–C(1) 1.961(13), Ga(2)–C(16) 1.992(11), Ga(3)–C(31) 1.987(12), Ga(4)–Ga(5) 2.4813(17), Ga(4)–Ga(6) 2.467(3), Ga(5)–C(46) 1.996(14), Ga(5)–C(61) 1.993(14), Ga(6)–C(76) 2.010(12); Ga(2)-Ga(1)-Ga(3) 116.17(5), Ga(2)-Ga(1)-Ga(2A) 127.65(10), Ga(5)-Ga(4)-Ga(6) 115.34(5), Ga(5)-Ga(4)-Ga(5A) 129.32(10).

In summary, double reduction of $Trip_2GaGaTrip_2$ leads to $Na_2[Ga(GaTrip_2)_2]_3$ by an as yet unknown pathway. Clearly, the rearrangement involves cleavage of Ga–C bonds and a stoichiometric reaction may be written in accordance with Equation (1). The first step of this reaction may involve double reduction to give the doubly reduced $Na_2[Trip_2GaGaTrip_2]$ which may eliminate an equivalent of NaTrip to afford a species of formula $Na[TripGaGaTrip_2]$. Indeed, a neutral species with a related composition, $RGaGaR_2$ ($R = Si(tBu)_3$), has been reported recently by Wiberg and co-workers.[9] However, the subsequent steps in the reduction to give **3** remain unknown at present.

$$4\,Na + 2\,Trip_2GaGaTrip_2 \longrightarrow Na_2[Ga(GaTrip_2)_3] + 2\,NaTrip \qquad (1)$$

Attempts to measure the Ga–Ga π bond strength in **3** by using variable-temperature ^1H NMR spectroscopy have not yet led to conclusive results. Nonetheless, both **3** and **4** display dynamic NMR behavior.[10] For **3** two dynamic processes with barriers near 14 and 18 kcal mol^{-1} were observed, whereas **4** displayed an energy barrier near 18 kcal mol^{-1}. If it is assumed that the latter value is associated with ring flipping, it is possible that the 18 kcal mol^{-1} value for **3** represents the same phenomenon. The 14 kcal mol^{-1} process in **3** may be associated with rotation around the Ga–Ga bonds. Since this must also involve rupture of the Na^+ ring interactions, which may be quite strong,[11] it is probable that Ga–Ga π bond strength is significantly less than this value.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

$\mathbf{3}\cdot 3\,C_6H_6$: Sodium (0.21 g, 9.1 mmol), cut into small pieces, was added to a solution of **1** (0.92 g, 0.96 mmol) in NEt_3 (40 mL) at room temperature. After about 20 h the solution had become a dark red-green color. After stirring the mixture for two more days, the solvent was removed under reduced pressure and the remaining dark brown, almost black, solid was extracted with *n*-hexane (ca. 80 mL). The dark red-green solution was then filtered through a sintered glass frit, concentrated to about 10 mL and cooled to −20 °C for one week to afford small black crystals. Recrystallization from benzene (3–4 mL) at 6 °C overnight gave 0.21 g of large (up to 6 mm) black crystals of $\mathbf{3}\cdot 3\,C_6H_6$ based on the stoichiometry in Equation (1). Yield: 25%. M.p. 190–200 °C. The compound loses some of the benzene of crystallization upon isolation and drying. UV/Vis (*n*-hexane): $\lambda(\varepsilon) = 850$ (9000), 422 nm (sh, 9000); ^1H NMR (C_7H_8, 60 °C): $\delta =$ 7.08 (br. s; *m*-H), 6.68 (br. s; *m*-H), 4.63 (br. s; *o*-CH), 3.19 (br. s; *o*-CH), 2.65 (sept, $^3J = 6.6$ Hz, *p*-CH) 1.63, 1.42, 1.27, 0.98, 0.79 (br. s; *o*-CH_3), 1.14 (d, $^3J = 6.6$ Hz; *p*-CH_3).

4: A solution of **3** (0.15 g, 0.1 mmol) in toluene (ca. 10 mL) was treated with dry air (11.0 mL, ca. 0.1 mmol 0_2) at 0 °C over a period of several hours in portions of 2 mL. The resulting red solution was concentrated to about 1–2 mL and cooled to −20 °C for three days to give small pale orange crystals of **4** which were washed with *n*-hexane (2 mL) and dried under reduced pressure. Yield: 50 mg (33%). Crystals suitable for X-ray structure analysis were obtained from a saturated benzene solution at 6 °C. M.p. 210–212 °C (decomp; melts and becomes black); ^1H NMR (C_7D_8): $\delta = 7.04$ (s, *m*-H; 6H), 6.95 (s, *m*-H; 6H), 3.03 (sept, 6H, $^3J = 6.6$ Hz; *o*-CH), 2.77 (sept, 12H, $^3J = 6.6$ Hz; *o*- and *p*-CH), 1.48 (d, 18H, $^3J = 6.6$ Hz; *o*-CH_3), 1.25 (d, 18H, $^3J = 6.6$ Hz; *o*-CH_3), 1.23 (d, 36H, $^3J = 6.6$ Hz; *p*-CH_3), 0.97 (d, 18H, $^3J =$ 6.6 Hz; *o*-CH_3), 0.60 (d, 18H, $^3J = 6.6$ Hz; *o*-CH_3). UV/Vis (*n*-hexane): λ (ε) = 348 nm (1200).

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[4] A simplified analysis of the π orbitals, assuming approximate D_3 point group symmetry for the Ga_4 array, affords two molecular orbitals (one bonding, one antibonding) of A_2 symmetry and two degenerate nonbonding orbitals of E symmetry. In **3** the bonding A_2 orbital is occupied by a pair of electrons, whereas in **4** it is unoccupied.

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Supramolecular Aggregates of Dendritic Cyclophanes (Dendrophanes) Threaded on Molecular Rods with Steroid Termini**

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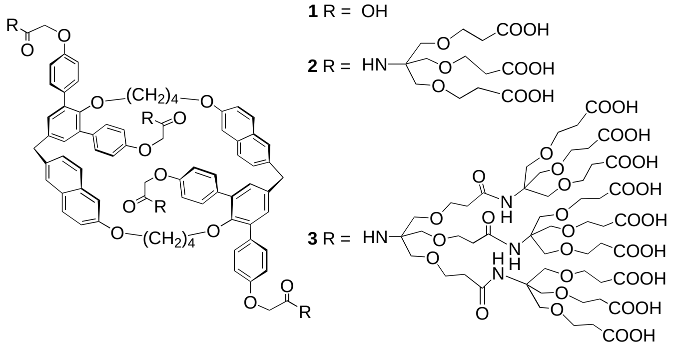
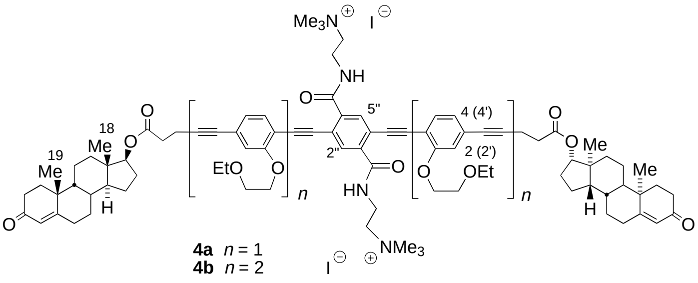
Noncovalent association of dendrimers[1] promises to provide a rapid, efficient way to construct higher molecular architectures with properties and functions[2] that are absent in the individual components. Whereas metal ion mediated assembly of dendritic branches (dendrons) to form higher generation compounds is well established,[1a, 3] the noncovalent networking[4a] of individual dendrimers to defined higher order structures in the absence of metal ions has only been achieved in a few cases.[4–7] A particularly intriguing example for dendritic self-association is the discrete hexameric assembly of dendritic wedges through directional COOH ··· COOH hydrogen-bonding interactions, which was reported by Zimmerman and co-workers.[6] Hydrophobic nonstoichiometric association of dendrimers in aqueous solution has been observed on several occasions,[5, 8] yet apolar bonding interactions and hydrophobic desolvation have not been previously employed to form structurally defined supramolecular aggregates containing two or more dendritic components. Here we report for the first time the formation of such assemblies in aqueous solution by hydrophobically driven threading of water-soluble dendrophanes (*dendri*tic cyclo*phanes*)[9] onto the testosterone termini of suitably designed molecular rods.

The initiator core cyclophane **1** (generation zero, G-0) and the two dendrophanes of the first (**2**, G-1; $M_r = 2486$) and second generation (**3**, G-2; $M_r = 6318$) had previously been shown to form stable 1:1 complexes (ΔG° at 298 K between -3.9 and -4.3 kcal mol^{-1}) with testosterone in borate-buffered D_2O (pD 10.5)/CD_3OD (1/1).[10] ^1H NMR investigation of the bonding provided clear evidence that the steroid binds axially in the cyclophane cavity of **2** or **3** rather than in nonspecific fluctuating voids in the dendritic shells.[11] The molecular rods **4a** and **4b** consist of rigid oligo(phenylacetylene) spacers with terminal testosterone units for dendrophane complexation. Because of their different lengths, they were expected to accommodate dendrophanes of different generation and size. Solubility of the rods in aqueous solutions represented a considerable challenge, which could be overcome with the attachment of both glycol ether groups and quaternary ammonium ions (to the central benzene ring). These ions were expected to undergo ion pairing with the





4a $n = 1$
4b $n = 2$

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