Protein expression, purification, and characterization: Plasmid pLEIZ was used to express the Z-domain gene with an amber codon at the seventh position under the control of a bacteriophage *T5* promoter and t_0 terminator, and the mutRNA$^{Tyr}_{CUA}$ gene under the control of the *lpp* promoter and *rrnC* terminator. The AL-TyrRS gene was encoded in plasmid pBK-ALRS under the control of the constitutive *E. coli* GlnRS promoter and terminator. *E. coli* DH10B cells cotransformed with pLEIZ and pBK-ALRS were grown in minimal media containing 1% glycerol and 0.3 mM leucine (GMML media) with 25 $\mu g\,mL^{-1}$ kanamycin, 34 $\mu g\,mL^{-1}$ of chloramphenicol, and 0.5 mM **2**. When cells reach an optical density (OD_{600}) value of 0.5, isopropyl-β-D-thiogalactopyranoside (IPTG; 1 mM) was added to induce protein expression. After 4 h, cells were pelleted and the protein was purified by Ni^{2+}-affinity chromatography according to the manufacturer's protocol under denaturing conditions (Quiagen, Valencia, CA). Proteins were then desalted by using a PD-10 column (Amersham Pharmacia, Piscataway, NJ) and eluted in water. The yield of protein was measured by Bradford assay (BCA kit, Biorad, Hercules, CA). Aliquots of protein were used for SDS-PAGE and mass spectroscopic analysis.

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Synthesis and Characterization of the Neutral "Digallene" Ar′GaGaAr′ and Its Reduction to $Na_2Ar'GaGaAr'$ (Ar′ = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-*i*$Pr_2C_6H_3$)[**]

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The publication of the remarkable gallium compound $Na_2Ar^*GaGaAr^*$ (**1**; Ar* = 2,6-$Trip_2C_6H_3$, Trip = 2,4,6-*i*$Pr_3C_6H_2$) in 1997 resulted in much controversy owing to the claim that it contained a Ga–Ga triple bond.[1] Initially, the triple bonding in this molecule was justified on the basis of a short Ga–Ga distance (2.319(3) Å) and the correspondence of the putative $[Ar^*GaGaAr^*]^{2-}$ ion to the neutral germanium species Ar*GeGeAr*—a germanium–alkyne analogue. Although the existence of Ga–Ga triple bonding has received support from some calculations,[2–6] others have questioned this view on the basis of 1) the *trans*-bent structure of the C_{ipso}-Ga-Ga-C_{ipso} array which indicates lone pair character at the gallium center,[7–11] 2) the Na–aryl ring[8] and Na–Ga interactions[11] which shorten the Ga–Ga distance, and 3) the role of the *para*-*i*Pr groups on the flanking aryl rings which cause Ga-Ga-C angular distortions that can strengthen the Ga–Ga bond.[11] Force constant calculations have also pointed to a relatively weak Ga–Ga interaction.[12, 13] The publication of the cluster species $K_2Ar^*Ga_4Ar^*$, which contains a Ga_4 ring with no Ga–Ga triple bonding as part of an octahedral K_2Ga_4 core, has underlined the importance of the alkali metal for the stability of **1**.[14] However, apart from this isolated report, all arguments regarding the Ga–Ga bonding in **1** have been grounded in calculations of various degrees of sophistication[2–11] and the original experimentally determined structural parameters.[1] In 1998 several experiments were suggested whose object was the elucidation of the important factors governing the nature of the Ga–Ga bond.[15] Among these were the investigation of the effects of changing or removing the alkali metal ions and the isolation and characterization of the neutral "digallene" species Ar*GaGaAr* which, should contain a Ga-Ga double bond if the assumption of triple bonding in **1** was correct. The former question has been partly answered through the synthesis of $K_2Ar^*Ga_4Ar^*$. However, no stable neutral Ga–Ga bonded dimers of the general formula RGaGaR (R = organic or related group) have yet been described. Calculations on a variety of model species, including HGaGaH,[10, 11, 16–19] MeGaGaMe,[9–11] and PhGaGaPh,[11] as well as IR spectroscopy of HGaGaH in a frozen matrix[19, 20] point to weak Ga–Ga bonding. It is now shown that the compound Ar′GaGaAr′ (**2**; Ar′ = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-*i*$Pr_2C_6H_3$), can be isolated and characterized with

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use of a terphenyl substituent (Ar′) that is closely related to the Ar* ligand employed in the synthesis of **1**.

Compound **2** was synthesized by the reaction of "GaI"[21] with LiAr′ in toluene in accordance with Equation (1).

$$\text{“GaI”} + \text{LiAr}' \xrightarrow[-78\,^{\circ}\text{C}]{\text{PhMe}} \text{Ar}'\text{GaGaAr}'\ (\mathbf{2}) + \text{I(Ar}')\text{GaGa(Ar}')\text{I}\ (\mathbf{3}) + \text{LiI} \qquad (1)$$

Green crystals of **2** and yellow crystals of **3** were each isolated in about 25 % yield from this reaction. The structure of **2** is illustrated in Figure 1 and consists of centrosymmetric Ga–Ga-bonded dimers with a planar, *trans*-bent C1-Ga1-Ga1A-C1A core.[22] The Ga–Ga and Ga–C distances are 2.6268(7) and 2.025(3) Å, respectively, and the Ga-Ga-C angle is 123.16(7)°. As is apparent from Figure 1, the plane of the central (C1) ring lies almost perpendicular (89.2°) to the C1-Ga1-Ga1A-C1A core and the flanking 2,6-$i\text{Pr}_2\text{C}_6\text{H}_3$ rings are almost perpendicular (89.8 and 85.7°) to the central ring. The structural parameters within the Ar′ ligand are normal and there are only slight deviations from expected values. The Ga–Ga distance is about 0.1 Å longer than the upper end of the single bond length range (2.33 – 2.54 Å)[23, 24] for digallanes and related compounds. It is also notably longer (by ca. 0.14 Å) than the Ga–Ga distance (2.493(2) Å) in **3**,[22] which has similar steric loading. However, it lies within the range (2.57 – 2.71 Å) observed in the Ga–Ga-bonded tetrahedrane clusters $(\text{GaR})_4$.[25] These clusters are electron deficient with a formal Ga–Ga bond order of ⅔ and were found to dissociate in hydrocarbon solutions—a fact that was interpreted in terms of an equilibrium between monomers and tetramers. The tetramers are also known to dissociate to monomers in the vapor phase as shown by mass spectrometry and electron diffraction studies.[29, 30] Similarly, compound **2** is partly dissociated to monomers in solution, and cryoscopic (cyclohexane) molecular weights that lie between those expected for monomers and dimers were observed at a concentration of 6 mmolal. It also sublimes readily at 150 °C at a pressure of 0.05 mm Hg, suggesting a monomeric structure in the vapor phase. The structural and physical data for **2** thus point to species that has relatively weak Ga–Ga bonding and a bond order that is significantly less than unity.[10]

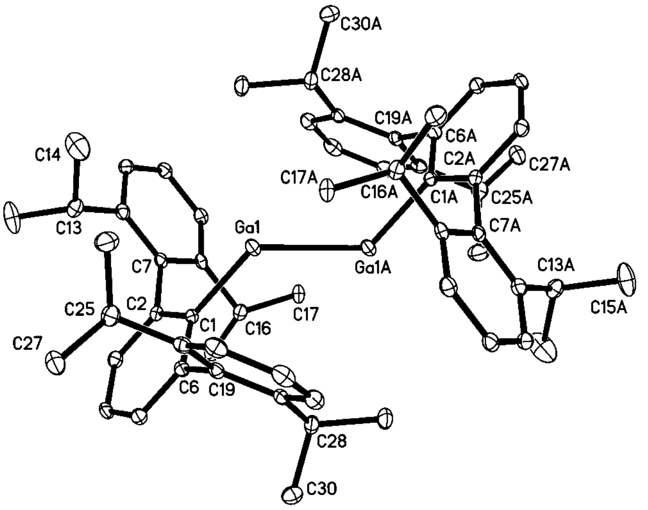

Figure 1. Structure of **2** (thermal ellipsoid plot; H atoms are not shown). Bond lengths [Å] and angles [°]: Ga1-Ga1A 2.6268(7), Ga1-C1 2.025(3), C1-C2 1.402(6), C1-C6 1.412(4); C1-Ga1-Ga1A 123.16(7), Ga1-C1-C2 122.6(2), Ga1-C1-C6 119.2(2), C1-C2-C6 118.2(3).

The sodium derivative $\text{Na}_2\text{Ar}'\text{GaGaAr}'$ (**4**) can be isolated as dark red crystals from the reduction of **2** or **3** with sodium metal in diethyl ether. This reaction establishes a direct connection between the neutral **2** and the doubly reduced **4**.

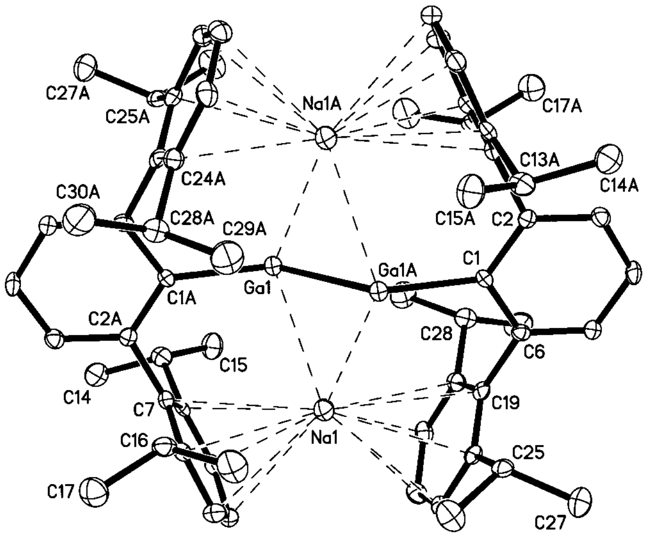

Figure 2. Structure of **4** (thermal ellipsoid plot; H atoms are not shown). Bond lengths [Å] and angles [°]: Ga1-Ga1A 2.347(1), Ga1-C1 2.059(5), Ga1-Na1 3.058(2), Ga1-Na1 3.101(2), Ga-Na 2.879(6)-3.051(5) (av 2.97(5)); Ga-Ga1A-C1 130.7(1), Na1-Ga1-Na1A 135.21(3).

Compound **4**, the structure[22] of which is illustrated in Figure 2, crystallizes as centrosymmetric molecules that feature a planar, *trans*-bent C1-Ga1-Ga1A-C1A core with sodium atoms that are complexed by Dipp rings and which almost symmetrically bridge the gallium atoms on each side of the C1-Ga1-Ga1A-C1A plane. The Ga–Ga and Ga–C distances are 2.347(1) and 2.059(5) Å, respectively, and the Ga-Ga-C angle is 130.7(1)°. The Ga–Na distances are 3.058(2) and 3.101(2) Å and the average Na–C(ring) distance is 2.97(5) Å. Most of these structural parameters are very similar to those previously reported for the structure of **1**[1, 14] for which the following values were determined: Ga–Ga 2.319(3), 2.324(1) Å; Ga–C(av) 2.044(16), 2.041(4) Å; Ga-Ga-C(av) 131.0(2.5), 130.7(1)°; Ga–Ga(av) 3.081(14), 3.084(19) Å; Na–C 3.04(2), 2.995(4) Å. The only parameter that shows a significant difference is the Ga–Ga distance, which in **4** is either 0.028[1] or 0.021 Å[14] longer than those reported for **1**. The Ga-Ga-C angle remains essentially unchanged so that, in this molecule at least, it does not correlate with the Ga–Ga distance as suggested by calculations on **1**. The reasons for the different Ga–Ga distances in **1** and **4** remain obscure. It should, however, be borne in mind that the Ga–Ga bond is weak and that changes in the aromatic substitution or molecular packing can affect the Ga–Ga bond length.

In summary the Ga–Ga bond in the "digallene" **2** is weak and the bond order is less than unity. Furthermore, the Ga–Ga bond order in the structurally uncharacterized Ar*-

substituted congener is likely to be lower than that in **2** owing to the greater steric crowding of the Ar* vis-a-vis the Ar′ substituent.[28–30] Numerous attempts[30] to crystallize a species of the formula GaAr* have been unsuccessful. However, the experimental evidence suggests that this compound will be either a monomer like its indium congener InAr*[29] or a weakly bonded dimer as suggested by calculations on model species such as PhGaGaPh.[11] In either case, the results point to a bond order of between one and two in the original $Na_2Ar^*GaGaAr^*$ species.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

2: A rapidly stirred slurry of "GaI" (1.49 g, 7.60 mmol) in toluene (20 mL),[21] cooled to about −78 °C, was treated dropwise with a solution of $(LiAr')_2$ (3.07 g, 3.80 mmol) in toluene (40 mL) over about 1 h, after which time the mixture was allowed to come to room temperature over a period of 6 h. Stirring was discontinued and the suspension was allowed to settle. The dark green supernatant solution was filtered through Celite and concentrated to about 15 mL whereupon a yellow-orange precipitate formed. This was allowed to settle and the solution was separated by decantation. The yield of the orange-yellow solid, which is almost pure **3**, is 1.10 g (0.93 mmol, 24.4 %). The green supernatant liquid was stored in a freezer at about −20 °C for 12 h to afford a green crystalline solid. This was recrystallized from a minimum volume of warm hexane to afford the product **2** (0.90 g, 0.96 mmol; 25.3 %) as green crystals. M.p. 206–210 °C. Correct C,H analysis; ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.07$ (d, $^3J_{H,H} = 6.6$ Hz, 24 H; $CH(CH_3)_2$), 1.09 (d, $^3J_{H,H} = 6.6$ Hz, 24 H; $CH(CH_3)$), 2.98 (sept, $^3J_{H,H} = 6.7$ Hz, 8 H; $CH(CH_3)_2$), 7.02 (d, $^3J_{H,H} = 7.6$ Hz, 8 H; *m*-Dipp), 7.14, 7.19, 7.21 ppm (m, *p*-C_6H_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): $\delta = 25.01$ ($CH(CH_3)_2$), 25.37 ($CH(CH_3)_2$), 30.92 ($CH(CH_3)_2$), 123.03 (*p*-C_6H_3), 123.40 (*m*-Dipp), 128.20 (*m*-C_6H_3), 128.80 (*i*-Dipp), 138.87 (*o*-C_6H_3), 144.72 (*p*-Dipp), 147.16 (*o*-Dipp), 173.80 ppm (*i*-C_6H_3); UV/Vis (hexanes): λ_{max} (ε) = 350 (990), 437 nm (430 $mol\,L^{-1}\,cm^{-1}$). **3**: Yield: 1.08 g, 0.91 mmol; m.p. > 260 °C (decomp); ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 0.99$ (d, $^3J_{H,H} = 6.4$ Hz, 24 H; *o*-$CH(CH_3)_2$), 1.18 (d, $^3J_{HH} = 6.4$ Hz, 24 H; *o*-$CH(CH_3)_2$), 2.96 (sept, $^3J_{H,H} = 6.4$ Hz, 8 H; *o*-$CH(CH_3)_2$), 7.11–7.15 (m, *m*-C_6H_3, *m*-, *p*-Dipp), 7.29 ppm (t, $^3J_{H,H} = 7.6$ Hz, 2 H, *p*-C_6H_3); $^{13}C\{^1H\}$ (100.6 MHz, C_6D_6, 25 °C): $\delta = 25.43$ (*o*-$CH(CH_3)_2$), 26.83 (*o*-$CH(CH_3)_2$), 31.23 (*o*-$CH(CH_3)_2$), 123.39 (*p*-C_6H_3), 124.58 (*m*-Dipp), 129.83 (*i*-Dipp), 130.60 (*m*-C_6H_3), 140.40 (*o*-C_6H_3), 145.36 (*p*-C_6H_3), 148.07 (*o*-Dipp), 152.12 ppm (*i*-C_6H_3).

4: A solution of **2** (1.02 g, 1.9 mmol) in diethyl ether (30 mL) was added to sodium metal (0.30 g, 13 mmol) and stirred for 4 h at 25 °C during which time the color changed from green to dark purple. The solution was separated from the excess sodium, concentrated, and cooled in a freezer at −20 °C for 30 h to afford **4** as dark red parallelepipeds. Yield: 0.37 g, 38 % M.p. 121–123 °C (decomp > 270 °C); ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 1.12$ (d, $^3J_{H,H} = 6.8$ Hz, 24 H; $CH(CH_3)_3$), 1.14 (d, $^3J_{H,H} = 6.8$ Hz, 24 H; $CH(CH_3)_2$, 2.90 (sept, $^3J_{H,H} = 6.8$ Hz, 8 H; $CH(CH_3)_2$), 7.10 (d, $^3J_{H,H} = 8.0$ Hz, 4 H; *m*-C_6H_3), 7.18 (d, $^3J_{H,H} = 8.0$ Hz, 8 H; *m*-Dipp), 7.21 (t, $^3J_{H,H} = 8.0$ Hz, 2 H; *p*-C_6H_3), 7.31 ppm (t, $^3J_{H,H} = 7.6$ Hz, 4 H; *p*-Dipp); $^{13}C\{^1H\}$ NMR (150.6 MHz, C_6D_6, 25 °C): $\delta = 24.31$ ($CH(CH_3)_2$), 24.43 ($CH(CH_3)_2$), 30.72 ($CH(CH_3)_2$), 122.82 (*p*-C_6H_3), 128.19 (*m*-Dipp), 128.37 (*m*-C_6H_3), 131.39 (*p*-Dipp), 139.65 (*o*-C_6H_3), 141.04 (*i*-Dipp), 146.82 (*o*-Dipp), 149.25 ppm (*i*-C_6H_3); UV/Vis (hexanes): λ_{max} (ε): 342 (2700), 439 (1500), 528 nm (1200 $mol\,L^{-1}\,cm^{-1}$).

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[22] Crystallographic data for **2**–**4**: Recorded at 90 K with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation: **2**: $a = 9.1819(9)$, $b = 12.7082(13)$, $c = 13.0454(13)$ Å, $\alpha = 109.856(2)$, $\beta = 98.329(2)$, $\gamma = 110.940(2)°$, triclinic, space group $P\bar{1}$, $Z = 1$, $R1 = 0.0477$ for 5131 ($I > 2\sigma(I)$) data; **3**: $a = 17.059(9)$, $b = 14.668(7)$, $c = 22.259(16)$ Å, $\beta = 101.88(4)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $R1 = 0.0653$ for 5732 ($I > 2\sigma(I)$) data; **4**, $a = 11.487(3)$, $b = 18.054(4)$, $c = 13.413(4)$ Å, monoclinic, space group $P2_1/n$, $Z = 2$, $R1 = 0.0498$ for 2371 ($I > 2\sigma(I)$) data. CCDC-186153 (**2**), CCDC-186154 (**3**), CCDC-186155 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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