Reactions of Tetrakis[bis(trimethylsilyl)methyl]digallane(4) with Carboxylic Acids – Substituent Exchange and Bridging of the Ga–Ga Bond by Two Carboxylato Groups☆

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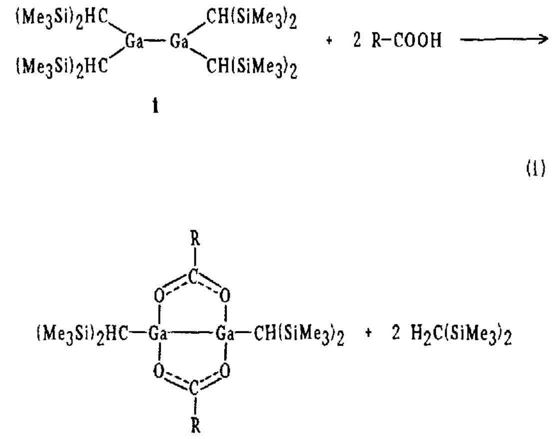
Yellow tetrakis[bis(trimethylsilyl)methyl]digallane(4) **1** reacts with two equivalents of the carboxylic acids RCOOH (R = $-C_6H_5$, $-p-BrC_6H_4$, $-3,5-Me_2C_6H_3$, $-CMe_3$) to yield almost quantitatively colorless products in which two bis(trimethylsilyl)methyl groups are replaced by two carboxylato ligands. As shown by a crystal structure determination with the 4-bromo-phenyl derivative (**3**), the Ga–Ga bond is bridged by both carboxylato groups in a chelating manner. The Ga–Ga distance is shortened to 238.5(2) pm (**1**: 254.1(1) pm) and the coordination number of the Ga atoms increased to four.

Organoelement compounds with Al–Al[1,2], Ga–Ga[3–8], and In–In bonds[9,10] show a remarkable chemical reactivity. Up to now five different types of reactions have been observed: (i) insertion of molecules and atoms into the element–element bonds[11]; (ii) electron transfer with the formation of radical anions exhibiting one-electron element–element π bonds[2,4,12]; (iii) formation of adducts with terminally coordinated Lewis bases[13]; (iv) metathesis reactions[14], and (v) deprotonation reactions in the particular case of the C–H acidic bis(trimethylsilyl)methyl derivatives with the formation of five-membered heterocycles[15]. In the course of our investigations the question arose, whether or not the replacement of the alkyl substituents could be achieved by the reaction with protic reagents like alcohols or carboxylic acids without breaking the element–element bonds. We have started with reactions of carboxylic acids; we hoped that they could prevent the expected disproportionation by a chelating coordination and hence coordinative saturation of the Ga atoms.

Reactions of 1 with Carboxylic Acids

When a yellow solution of the digallane(4) **1**[3] was treated with the stoichiometric amount of a carboxylic acid, only one half of the starting compound was consumed. Complete reaction occurred with the molar ratio of only 1 to 2, and two equivalents of bis(trimethylsilyl)methane were released each formula unit of **1** as detected by NMR spectroscopy. The carboxylic acids RCOOH employed were aromatic derivatives with R = phenyl, *p*-bromophenyl, and 2,6-dimethylphenyl, as well as the aliphatic pivalic acid; no significant difference in their reactivity towards compound **1** could be detected (eq. 1). Colorless solutions were formed, from which colorless crystals of the products were isolated in over 90% yield. Only the *tert*-butyl derivative **5** could not be purified by recrystallization from several noncoordinating solvents (*n*-pentane, *cyclo*-pentane, *n*-hexane, toluene); it was isolated from the reaction mixture in an analytical pure form as a high viscous liquid.



R		R	
$-C_6H_5$	2	$-3,5-C_6H_3Me_2$	4
$-4-Br-C_6H_4$	3	$-CMe_3$	5

All products (**2** to **5**) give the correct formula mass by the cryoscopical molar mass determination. They exhibit singlets for the $SiMe_3$ groups in both the ^1H and ^{13}C-NMR spectra. The inner protons of the substituents are shifted to high field [$\delta = -0.04$ to -0.15 (**2** to **4**) and 0.25 (**5**)] compared to **1** ($\delta = 1.11$), which is characteristic of bis(trimethylsilyl)methylgallium derivatives with tetracoordinated Ga atoms[16]. Similarly, the resonances of the α carbon atoms in the ^{13}C-NMR spectra show a shift to about $\delta = 5$ (**1**: $\delta = 25.9$) clearly indicating, that the carboxylato groups are bound in a chelating manner with both oxygen atoms coordinated to Ga. The CO_2 stretching vibration ($\nu_{as}CO_2$) in the IR spectra could be detected at about 1535 cm^{-1}. While **1** is deep yellow with a broad absorption at 360 nm in the UV/vis spectrum characteristic of Al–Al, Ga–Ga, and In–In bonds[3,9], the digallium compounds **2** to **5** are colorless showing no absorption in that region. This difference probably results from coordinative saturation of the gallium atoms and confirms that the color of the tetraalkyldigallium compound **1** as well as the dialuminium or diindium analogs is caused by a transition involving the empty p orbitals of the Ga atoms or the π orbital of the element–element bond.

The substitution reactions described are the first to be observed with tetraalkyldielement derivatives of the elements of the third main-group. They are important for the syntheses of further derivatives and are the starting point for a very interesting and quite new chemistry. The Al and In analogs do not give similar reactions on treatment with carboxylic acids, probably due to the more electropositive character of these elements, and bis(trimethylsilyl)methane is formed as a by-product only in trace amounts. At least two unknown products could be detected by NMR spectroscopy, which we were not able to separate and to identify up to now. It seems however, that the element–element bond is cleaved in the course of these reactions.

Crystal Structure of 3

The molecular structure of **3** (Figure 1) exhibits two carboxylato groups bridging the Ga–Ga bond in a butterfly arrangement with an eclipsed conformation and torsion angles of the Ga–O bonds of 1.2° (O1–Ga1–Ga2–O2) and 0.6° (O3–Ga1–Ga2–O4). The Ga–C bonds deviates more significantly from the ideal position with a torsion angle C1–Ga1–Ga2–C2 of 8.4°. The Ga–O bonds are approximately perpendicular to the Ga–Ga axis (Ga–Ga–O 88.0° on average), and the angle between the normals of both planes Ga_2O_2C of the gallium carboxylato groups amount to 85.7°. Surprisingly, the Ga–Ga–C angles approach linearity (158.2° on average).

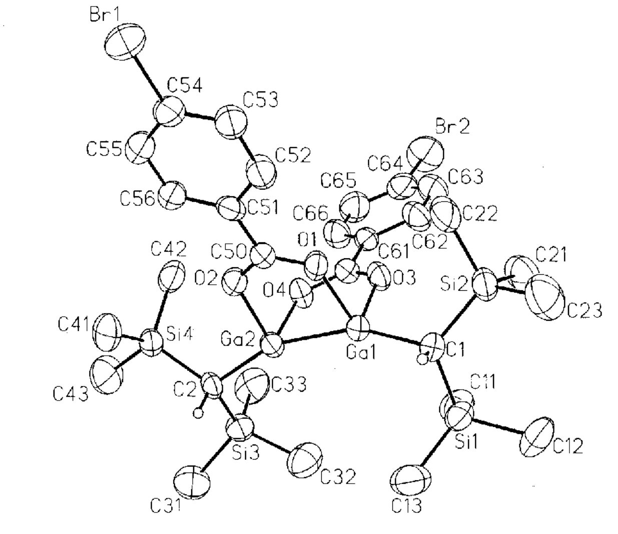


Figure 1. Molecular structure of **3**; the ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: Ga1–Ga2 238.5(2), Ga1–C1 195.5(8), Ga2–C2 195.8(8), Ga1–O1 200.4(6), Ga1–O3 200.4(6), Ga2–O2 202.7(6), Ga2–O4 201.0(6), Ga1–Ga2–C2 158.7(3), Ga2–Ga1–C1 157.7(3), Ga1–Ga2–O2 87.5(2), Ga1–Ga2–O4 88.0(2), Ga2–Ga1–O1 88.4(2), Ga2–Ga1–O3 87.9(2), O1–Ga1–O3 93.7(3), O2–Ga2–O4 93.1(3), C50–O1–Ga1 120.0(5), C50–O2–Ga2 119.7(5), C60–O3–Ga1 120.2(6), C60–O4–Ga2 119.8(6)

The Ga–O bond lengths (201.1 pm on average) are in that region usually observed for Ga–O bonds between tetracoordinated Ga atoms and oxygen as a part of a delocalized electronic system[17], and the Ga–C bond lengths are shortened to 195.7 pm with respect to the starting compound **1** (199.6 pm[3]). The Ga–Ga bond in **3** is very short [238.5(2) pm]. We observed a much longer Ga–Ga bond length in **1** with 254.1(1) pm[3], which is similar observed in tetraaryl or tetraamido derivatives[4,6]. Tetraalkyl or tetraaryl radical anions $[R_2Ga\div GaR_2]^-$ with a 1-electron Ga–Ga π bond exhibit bonds as short as in **3** with 240.1[12] or 234.2 pm[4]. Inorganic compounds with electronegative substituents like halides[18] or chalcogenides[19] and a Ga–Ga single bond show values of about 240 pm comparable to compound **3**. Very short Ga–Ga bonds were recently observed with digallium derivatives bearing two carbaborate [234.0(1) pm][7] or two unsaturated diamide ligands [233.3(1) pm][8]. The reason for the dramatic shortening of the Ga–Ga bond compared to the starting compound **1** may be (i) the coordination by the electronegative oxygen atoms, and (ii) the bridging by the chelating substituents. In view of the almost linear Ga–Ga–C angles, it could also be interpreted in terms of an unusual hybridization with an interaction of two sp hybridized Ga with four oxygen donor atoms; a similar description including, however, a σ-donor/π-acceptor bond is given for three-membered heterocycles (e.g. R_2B_2O or R_4Si_2O[20]).

The Ga_2O_2C heterocycles in **3** are almost ideally in one plane with the phenyl groups of the carboxylato substituents, and the angles between the normals of the planes amount to 2.6° (C50–C51) and 5.4° (C60–C61). The C–O (127 pm on average) as well as the C50–C51 and C60–C61 bond lengths between the carboxylato and the *ipso*-C atoms (147 pm) are as expected[21]. The bis(trimethylsilyl)methyl gallium groups adopt a conformation, in which one C–Si bond is arranged in an antiperiplanar manner to one of the Ga–O bonds (torsion angles O1–Ga1–C1–Si1 167.4° and O2–Ga2–C2–Si3 164.5°). The corresponding C–Si bonds (C1–Si1 and C2–Si3) are lengthened by 2 to 3 pm in comparison to the remaining C–Si bonds, which show an approximately synclinal arrangement to Ga–O bonds (O3–Ga1–C1–Si2 39.5° and O2–Ga2–C2–Si4 29.5°). The bridging of an element–element bond by a carboxylato group has to our knowledge not been observed before in main-group chemistry, while many such compounds are known with transition metals[22].

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Experimental

All procedures were carried out under purified argon in dried solvents (*n*-pentane with $LiAlH_4$, toluene and benzene with Na/benzophenone). Compound **1** was prepared as described in ref.[3]; the carboxylic acids from Aldrich were sublimed in vacuo for purification.

General Procedure for the Syntheses of Compounds **2** *to* **5**: Digallane(4) **1** (~0.5 g) was dissolved in 40 ml of *n*-pentane, cooled to −40 °C and treated with two equivalents of the carboxylic acid by the dropwise addition of a solution in 15 ml of toluene (pivalic acid in 15 ml of *n*-pentane). The mixture was warmed to room temp. and stirred for 4 to 12 h. The color changed from yellow to colorless. After evaporation of the solvent and $H_2C(SiMe_3)_2$ the residue was recrystallized from *n*-pentane (20/−50 °C).

Characterization of **2** *($R = C_6H_5$):* Yield: 97%; colorless, slightly air-sensitive crystals; m.p. (closed capillary, argon) 105 °C. – ^1H NMR (C_6D_6; 300 MHz; 300 K): $\delta = 8.29$ (pseudo d, *o*-H of phenyl), 6.99 (multiplet, *m*/*p*-H of phenyl), 0.40 ($SiMe_3$), −0.13 (GaCH). – ^{13}C NMR (C_6D_6; 75.5 MHz): $\delta = 177.7$ (CO_2), 133.5 131.6, and

130.8 (phenyl), 4.9 (GaCSi$_2$), 3.5 (SiMe$_3$). – IR (CsBr): $\tilde{\nu}$ = 1925 cm^{-1} vw, 1856 vw, 1794 vw, 1636 w, 1589 s (phenyl); 1532 s, 1458 w νCO$_2$; 1400 vs, 1375 sh, 1306 vw, 1279 vw, 1258 m, 1248 s δCH$_3$; 1173 m, 1140 w, 1105 vw, 1071 m νCC; 1013 vs δCH; 945 w, 845 vs, 770 vs, 729 w, 714 w ρCH$_3$(Si); 687 m, 675 m ν_{as}SiC; 627 w, 613 w ν_sSiC; 583 vw, 527 s, 469 w νGaC; 357 vw, 332 w δSiC. – $C_{28}H_{48}Ga_2O_4Si_4$ (700.5): calcd. C 48.0, H 6.9, Ga 19.9; found C 47.7, H 6.9, Ga 20.0. – Mol. mass: 701 (cryoscopically in benzene).

Characterization of **3** *(R = p-Br-C$_6$H$_4$):* Yield: 89%; colorless, slightly air-sensitive crystals; m.p. (closed capillary, argon) 125–127°C. – ^{1}H NMR (C$_6$D$_6$; 300 MHz; 300 K): δ = 7.88 (d, *o*-H of phenyl), 7.03 (d, *m*-H of phenyl), 0.37 (SiMe$_3$), –0.15 (GaCH). – ^{13}C NMR (C$_6$D$_6$ 75.5 MHz): δ = 177.0 (CO$_2$), 132.1 and 132.0 (*o/m*-C of phenyl), 130.1 and 129.0 (*p/i*-C of phenyl), 5.0 (GaCSi$_2$), 3.4 (SiMe$_3$). – IR (paraffin, CsBr): $\tilde{\nu}$ = 1923 cm^{-1} vw, 1842 vw, 1793 vw, 1588 m (phenyl); 1532 m νCO$_2$; 1460 vs, 1400 s, 1375 vs δCH$_3$ (paraffin); 1306 w, 1279 w, 1256 sh, 1248 m δCH$_3$; 1173 w, 1155 w, 1140 w, 1105 vw, 1071 w νCC; 1013 vs δCH; 945 w, 847 vs, 772 m, 721 m, 714 w ρCH$_3$(Si); 687 vw, 673 w ν_{as}SiC; 627 vw, 613 vw ν_sSiC; 527 m, 467 w νGaC; 357 vw, 332 w δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 255 nm (3.7). – $C_{28}H_{46}Br_2Ga_2O_4Si_4$ (858.3): calcd. C 39.2, H 5.4, Ga 16.2; found C 38.9, H 5.3, Ga 16.1. – Mol. mass: 775 (cryoscopically in benzene).

Characterization of **4** *(R = 3,5-Me$_2$C$_6$H$_3$):* Yield: 96%; colorless, slightly air-sensitive crystals; m.p. (closed capillary, argon) 162–163°C. – ^{1}H NMR (C$_6$D$_6$; 300 MHz; 300 K): δ = 8.00 (*o*-H of phenyl), 7.76 (*p*-H of phenyl), 2.02 (CH$_3$ of phenyl), 0.42 (SiMe$_3$), –0.04 (GaCH). – ^{13}C NMR (C$_6$D$_6$; 75.5 MHz): δ = 178.1 (CO$_2$), 138.1 and 135.3 (*o/m*-C of phenyl), 131.6 (*p/i*-C of phenyl), 21.0 (CH$_3$ of phenyl), 4.7 (GaCSi$_2$), 3.5 (SiMe$_3$). – IR (paraffin, CsBr): $\tilde{\nu}$ = 1927 cm^{-1} vw, 1818 vw, 1790 vw, 1603 w (phenyl); 1537 m νCO$_2$; 1462 vs, 1420 s, 1395 vs, 1377 vs δCH$_3$ (paraffin); 1310 m, 1271 s, 1260 s, 1246 s δCH$_3$; 1169 w, 1155 w, 1140 w, 1125 w, 1076 vw νCC; 1017 s δCH; 922 m, 862 sh, 845 vs, 791 s, 766 s, 721 s ρCH$_3$(Si); 687 sh, 677 s ν_{as}SiC; 623 w, 611 w ν_sSiC; 550 w, 519 w, 492 sh, 476 m νGaC; 342 vw, 284 m δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 250 nm (3.7), 290 (3.6). – $C_{32}H_{56}Ga_2O_4Si_4$ (756.6): calcd. C 50.8, H 7.5, Ga 18.4; found C 50.4, H 7.5, Ga 18.3. – Mol. mass: 716 (cryoscopically in benzene).

Characterization of **5** *(R = CMe$_3$):* Yield: 92%; colorless, slightly air-sensitive, highly viscous and spectroscopically pure liquid, which was characterized without further purification. – ^{1}H NMR (C$_6$D$_6$; 300 MHz; 300 K): δ = 1.15 (CMe$_3$), 0.30 (SiMe$_3$), 0.25 (GaCH). – ^{13}C NMR (C$_6$D$_6$; 75.5 MHz): δ = 191.3 (CO$_2$), 39.7 (CMe$_3$), 27.5 (C*Me*$_3$), 4.0 (GaCSi$_2$), 3.3 (SiMe$_3$). – IR (CsBr): $\tilde{\nu}$ = 1636 w, 1611 w, 1570 sh, 1535 s νCO$_2$; 1485 m δCH$_3$; 1458 w νCO$_2$; 1424 m, 1398 w, 1379 w, 1364 w, 1341 w, 1248 s, 1223 s δCH$_3$; 1015 m δCH; 964 vw, 941 vw, 893 vw, 862 sh, 841 vs, 785 w, 760 w, 729 vw ρCH$_3$(Si), νC$_3$C; 687 sh, 675 w ν_{as}SiC; 615 w ν_sSiC; 513 w νGaC; 438 w δC$_3$C; 322 vw δSiC. – $C_{24}H_{56}Ga_2O_4Si_4$ (660.5): calcd. C 43.6, H 8.5, Ga 21.1; found C 43.2, H 8.5, Ga 21.2. – Mol. mass: 620 (cryoscopically in benzene).

Crystal Structure Determination of **3**: Crystals of **3** by crystallization from *n*-pentane; $C_{28}H_{46}Br_2Ga_2O_4Si_4$; crystal size 0.5 × 0.4 × 0.4 mm; four-circle diffractometer Siemens P4; ω scan; temperature 20°C; triclinic $P\bar{1}$ (Nr. 2[23]); a = 1198.8(3), b = 1273.7(3), c = 1485.9(7) pm, α = 76.94(2)°, β = 87.89(3)°, γ = 63.70(2)°; V = 1976 · 10^{-30} m^3; $d_{calcd.}$ = 1.442 g/cm^3; Z = 2; 2Θ range 3.6 ≤ 2Θ ≤ 44°; μ(Mo-K_α) = 3.53 mm^{-1}, numerical absorption correction; 3342 independent reflections; 362 parameters; programs SHELXTL PLUS and SHELXL-93[24]; structure solution by direct methods; refinement by the full-matrix least-squares method with all independent structure factors; wR^2 = 0.144 (all data); R_1 = 0.0530 for 3275 $F > 4\sigma(F)$; max./min. residual electron density 0.55/–0.62 · 10^{30} e/m^3[25].

☆ Dedicated to Prof. Dr. *Walter Siebert*, on the occasion of his 60th birthday.

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