

Gallium-Gallium Single Bonds Terminally Coordinated by Tropolonato Ligands

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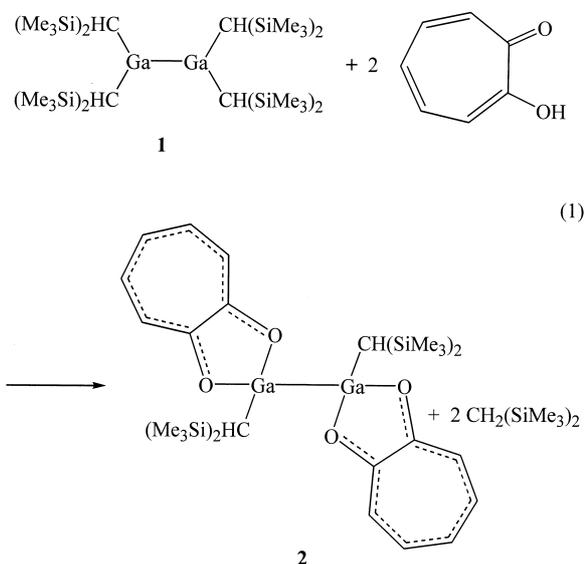
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Gallium, Tropolonato Complexes, Gallium-Gallium Bonds

Tetrakis[bis(trimethylsilyl)methyl]digallane(4) (**1**) reacted with tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) by replacement of two bis(trimethylsilyl)methyl groups and retention of its Ga-Ga single bond. Each gallium atom of the centrosymmetric product (**2**) is chelated by a tropolonato ligand. The Ga-Ga bond length (244.9 pm) is in the characteristic range of unsupported Ga-Ga bonds.

Introduction

The first organogallium compound containing a Ga-Ga single bond, $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ga-Ga}[\text{CH}(\text{SiMe}_3)_2]_2$ (**1**), was synthesized in our group by treatment of $\text{Ga}_2\text{Br}_4 \cdot 2$ dioxane with $\text{LiCH}(\text{SiMe}_3)_2$ in 1989 [1]. In contrast to Al-Al [2] and In-In bonds [3], the Ga-Ga bond was not cleaved in reactions of **1** with carboxylic acids. Instead, substituent exchange occurred, and two alkyl groups were replaced by chelating carboxylato ligands [4, 5]. Remarkably, these ligands adopted bridging positions across the Ga-Ga bonds as previously observed in transition metal chemistry. Macrocyclic compounds with up to 36 atoms comprising four Ga-Ga bonds were isolated in high yields by employing bifunctional dicarboxylic acids [6]. These macrocycles showed interesting supramolecular structures with inclusion of solvent molecules, for instance. In contrast to carboxylato groups, triazenido ligands occupied terminal positions [7]. The different coordination behaviour is readily understood, it depends on the distances between the coordinating atoms (bite) and the angle at the inner atom of the chelating ligand [5]. The deformation of that angle to small values is easier for the triazenido ligand, which favours its terminal arrangement. A similar bridging *versus* terminal coordination mode was observed for five atomic ligands such as imidotetraphenyldiphosphinato and iminotetraphenyldithiodiphosphinato, of which the dithio ligand coordinates the gallium atoms in a terminal position [8]. Four-atomic ligands have not



been studied up to now, and we hoped to realize substituent exchange by the treatment of **1** with tropolone.

Preparative Results

The reaction of two equivalents of colourless tropolone with the yellow digallium compound **1** gave a deep yellow solution, from which yellow crystals of the product **2** were obtained in 83% yield by slow evaporation of the solvent at room temperature (eq. (1)). The increase in coordination number of the gallium atoms caused a shift of the NMR resonances of the inner C-H groups to high

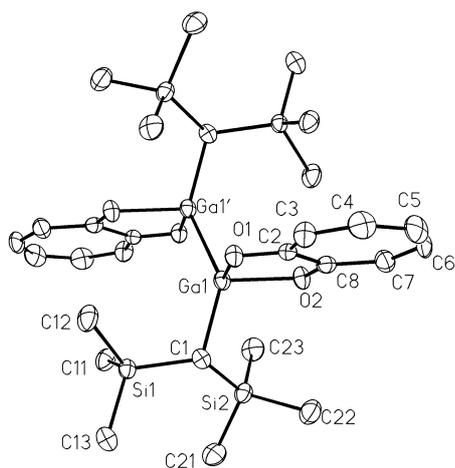


Fig. 1. Molecular structure of compound 2. The ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ga1-Ga1' 244.9(1), Ga1-O1 195.9(3), Ga1-O2 196.0(3), Ga1-C1 200.9(5), O1-Ga1-O2 81.5(1), C1-Ga1-Ga1' 130.9(2), O1-Ga1-Ga1' 110.5(1), O2-Ga1-Ga1' 109.3(1); Ga1' was generated by $-x + 1, -y + 1, -z$.

field ($\delta(^1\text{H}) = -0.26$ and $\delta(^{13}\text{C}) = 12.9$) compared to the corresponding resonances of 1 ($\delta(^1\text{H}) = 1.11$ and $\delta(^{13}\text{C}) = 25.9$ [1]). Similar changes have been observed before in many secondary reactions of 1 [9, 10]. While most of the secondary products of 1 containing coordinatively saturated gallium atoms are colourless [9, 10], compound 2 is bright yellow according to a maximum in the UV/vis spectrum at 370 nm. The intense colour may be caused by transitions in the delocalized π -system of the ligand.

Crystal Structures

The molecular structure and numbering scheme of 2 is depicted in Fig. 1. 2 has a Ga-Ga single bond, which is located on a crystallographic inversion centre. Each gallium atom has a distorted tetrahedral coordination sphere and is attached to two oxygen atoms of a terminally coordinated, chelating tropolonato ligand, to the inner carbon atom of one organoelement substituent, and to the second gallium atom. The Ga-Ga distance (244.9(1) pm) is in the range usually observed for unsupported Ga-Ga bonds terminally coordinated by chelating ligands such as various acetylacetonates [10 - 13], iminotetraphenyldithiodiphosphinato [8] or diphenyltriazenido groups [7]. Shorter ones (238 pm on average) were detected for the di-

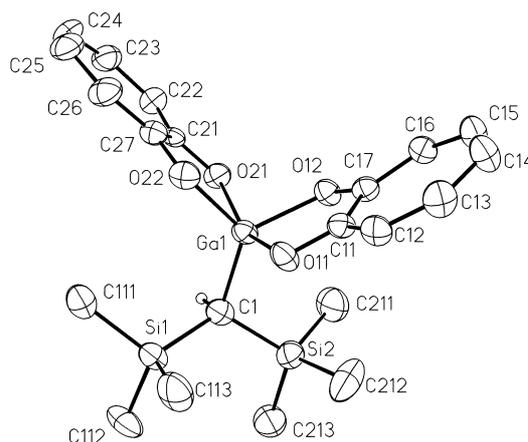


Fig. 2. Molecular structure of compound 3. The ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of H1 (arbitrary radius) are omitted. Selected bond lengths [pm] and angles [°]: Ga1-C1 196.3(8), Ga1-O11 201.6(6), Ga1-O2 192.8(5), Ga1-O21 204.1(6), Ga1-O22 193.5(6), C1-Ga1-O11 104.9(3), C1-Ga1-O12 125.9(3), C1-Ga1-O21 98.8(3), C1-Ga1-O22 124.0(3), O11-Ga1-O12 80.0(2), O11-Ga1-O21 156.3(2), O11-Ga1-O22 86.5(2), O12-Ga1-O21 86.6(2), O12-Ga1-O22 110.0(2), O21-Ga1-O22 79.8(2).

carboxylato compounds possessing bridged Ga-Ga bonds [4 - 6], and a longer bond was observed for the starting compound 1 (254.1 pm) [1]. The shortening may be caused by the reduced steric crowding in the molecules after replacement of two bulky substituents, by the coordination of electronegative atoms such as oxygen or nitrogen, and in the case of the carboxylato derivatives by the bridging of the E-E bonds. The Ga-O distances (196 pm on average) are shorter than those of the carboxylato bridged derivatives (201 pm), but correspond well to those of the terminally coordinated acetylacetonato compounds [10 - 13]. The bite of the tropolonato ligand (O...O 255.8 pm) is larger than that of the carboxylato groups (about 224 pm), but smaller than in the acetylacetonato derivatives (279 pm).

Some aspects of the different coordination behaviour have already been discussed [5]. The terminal coordination of the chelating ligands with a distorted tetrahedral coordination sphere at the gallium atoms is the most favourable configuration. But this particular form can only be realized by a significant deformation of the angle at the central atom of the chelating ligand (105.9° in the case of terminal triazenido groups [7]). In those cases in which the angle is large and invariable as with carboxy-

	2	3
Formula	C ₂₈ H ₄₈ Ga ₂ O ₄ Si ₄	C ₂₁ H ₂₉ GaO ₄ Si ₂
<i>M_r</i>	700.46	471.34
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> ; no. 14 [16]	<i>P</i> 1̄; no. 2 [16]
<i>a</i> (pm)	1024.2(4)	961.0(2)
<i>b</i> (pm)	1328.0(1)	1060.5(2)
<i>c</i> (pm)	1384.4(4)	1345.9(3)
α (°)	90	88.11(1)
β (°)	111.47(2)	73.33(1)
γ (°)	90	66.56(1)
<i>V</i> (Å ³)	1752.3(9)	1200.4(4)
ρ _{calc} (g cm ⁻³)	1.328	1.304
<i>Z</i>	2	2
<i>F</i> (000)	732	492
μ (Mo-K _α) (cm ⁻¹)	17.03	12.68
<i>T</i> (K)	193(2)	193(2)
Measured reflections	3250	10332
Unique reflections	3070 [<i>R</i> _{int} = 0.0533]	4336 [<i>R</i> _{int} = 0.0916]
Reflections <i>I</i> > 2σ(<i>I</i>)	2310	3748
Refined parameters	178	259
Final <i>R</i> values [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0574	<i>R</i> 1 = 0.0837
(all data)	<i>wR</i> 2 = 0.1610	<i>R</i> 2 = 0.2384
ρ _{fin} (max/min) (eÅ ⁻³)	0.981/-0.953	1.072/-0.760

Table 1. Crystallographic data for compounds 2 and 3.

$$^a R = \sum (||F_o| - |F_c||) / \sum |F_o|; wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}.$$

lato groups a terminal configuration would lead to a very short distance between the positively charged gallium and carbon atoms. This should result in a considerable repulsive interaction. The bridging form becomes more favourable, but it requires a re-hybridization of the gallium atoms with almost linear C-Ga-Ga groups and perpendicularly arranged chelating ligands. The interaction between gallium and oxygen in those compounds is essentially determined by pure *p*-orbitals of the gallium atoms in accordance with an sp-hybridization of gallium.

After isolation of 2 and concentration of the mother liquor, few single crystals of a second product (3) were obtained in some cases. Systematic changes in the excess of tropolone or in the reaction conditions such as temperature and reaction time did not result in an enrichment of that component. Crystal structure determination verified the cleavage of the Ga-Ga bond and the formation of the gallium(III) compound (Me₃Si)₂CH-Ga(O₂C₇H₅)₂ (3, Fig. 2) possessing two chelating tropolonato ligands. The gallium atom has coordination number five in a slightly distorted trigonal bipyramidal coordination sphere. The atoms Ga1, C1 of the bis(trimethylsilyl)methyl group as well as O12 and O22 of different tropolonato ligands are in the equatorial plane (sum of the angles 359.9°),

while the atoms O11 and O21 occupy the axial positions. The Ga-C (196.3(8) pm) and Ga-O bond lengths (193.2 pm) in the plane are in an expected range (see above), while the axial bonds Ga1-O11 and Ga1-O21 are lengthened (202.9 pm on average). Owing to the chelating coordination the axial oxygen atoms deviate from the ideal positions with an O11-Ga1-O21 angle of 156.3°. Only few tropolonato compounds of the trivalent elements of the third main group have been reported before [14].

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane over LiAlH₄). Digallane(4) (1) was synthesized according to a literature procedure [1]. Tropolone (Aldrich) was employed without further purification.

1,2-Bis[bis(trimethylsilyl)methyl]-1,2-di(tropolonato)-digallium (2)

A solution of digallane(4) (1) (0.210 g, 0.271 mmol) in 20 ml of *n*-pentane was added to a cooled (-70 °C) suspension of tropolone (0.069 g, 0.566 mmol) in 20 ml of *n*-pentane. The mixture was slowly warmed to room temperature and stirred for 14 h. A clear, bright yellow solution was formed. The solution was concentrated slowly (several days) at room temperature under slightly reduced pressure until a volume of about 2 ml was reached. A yel-

low, partially crystalline solid of **2** precipitated (0.158 g, 83%). Further concentration of the mother liquor gave few crystals of compound **3** in some cases. Characterization of **2**: Dec. p. (under argon, sealed capillary): 123 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.09 (4 H, d, ³J_{HH} = 11 Hz, H-3,7), 6.60 (4 H, dd, ³J_{HH} = 11 and 10 Hz, H-4,6), 6.20 (2 H, t, ³J_{HH} = 10 Hz, H-5), 0.33 (36 H, s, SiMe₃), -0.26 (2 H, s, GaCH). ¹³C NMR (C₆D₆, 100.6 MHz, 298 K): δ 179.5 (CO), 139.4 (C-3,7), 128.3 (C-4,6), 126.7 (C-5), 12.9 (Ga-C), 3.6 (SiMe₃). IR (cm⁻¹; paraffin; CsBr plates): 1597 m, 1521 m ν_{CC}, ν_{CO}; 1463 vs, 1377 vs paraffin; 1305 m, 1247 m δ_sCH₃; 1169 w, 1076 vw; 1016 m, 970 m ν_{CH}; 917 m, 844 s ρCH₃; 721 s paraffin; 669 w ν_{as}SiC₃ and ν_{CSi₂}; 610 w ν_sSiC₃; 564 w, 505 w, 464 vw, 414 w ν_{GaC}, ν_{GaO}. UV/vis (*n*-hexane): λ_{max}(log ε) = 240 (4.7), 320 (4.0), 370 (3.9).

Crystal structure determinations

Single crystals of compounds **2** and **3** were obtained by very slow (several days) concentration of solutions

in *n*-pentane at room temperature under slightly reduced pressure. Data collections were performed on a CAD-4 (2) or a STOE IPDS diffractometer (3) employing graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods and refined by full matrix least-squares calculations based on *F*² [15]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinements are given in Table 1. The crystallographic data of **2** and **3** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on quoting CCDC-168541 (2) and -168540 (3).

Acknowledgements

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