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Gallium–Gallium Bonds Bridged by Functionalized Carboxylato Ligands

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Dedicated to Professor Bernd Harbrecht on the Occasion of His 60th Birthday

Keywords: Gallium; Carboxylato ligands; Subvalent compounds; Gallium–gallium bonds; π Stacking

Abstract. Treatment of the tetraalkyldigallium compound R_2Ga–GaR_2 [R = CH($SiMe_3$)$_2$] (**1**) with a large number of different functionalized carboxylic acids afforded dicarboxylatodigallium compounds R_2Ga_2(μ-O_2C–R)$_2$, in which two carboxylato ligands bridge the Ga–Ga bonds. The chelating ligands have additional nitrogen, oxygen or phosphorus donor atoms and may be suitable to act as Lewis-bases to yield supramolecular aggregates in future investigations. Four compounds have been characterized by crystal structure determinations. One gave unprecedented dimeric formula units in the solid state by Ga–N interactions. The similar reaction with isonicotinic acid resulted in the cleavage of the Ga–Ga bond. A tetragallium compound was formed in which four isolated metal atoms were bridged by four organic ligands to give a square molecular core.

Introduction

The facile synthesis of the first organoelement compounds with Al–Al, Ga–Ga or In–In single bonds, R_2E–ER_2, was a mile-stone in Group 13 chemistry [1–3]. These compounds were stabilized by four bulky bis(trimethylsilyl)methyl groups and initiated broad research activities in that field [4]. They showed a singular chemical reactivity and many unprecedented secondary products have been isolated. Insertion reactions succeeded with atoms and molecules, deprotonation of the C–H acidic bis(trimethylsilyl)methyl groups gave a heterocyclic compound, electron transfer yielded radical anions containing 1e-E–E π-bonds, a metathesis reaction afforded a monomeric gallium telluride, and adducts were formed with suitable neutral or anionic donor ligands [5]. Substituent exchange reactions by retention of the E–E bonds are particularly interesting. However, the treatment of the dialuminum and diindium compounds with protic reagents gave exclusively cleavage of the E–E bonds [6], and only the reaction of the digallium compound R_2Ga–GaR_2 [R = CH($SiMe_3$)$_2$] (**1**) with carboxylic acids, acetylacetone derivatives, or diphenyltriazene resulted in the replacement of two alkyl groups [5, 7]. The dicarboxylatodigallium compounds (**2**, Scheme 1) exhibit a unique molecular structure, in which the Ga–Ga bonds were bridged by two chelating groups in a perpendicular arrangement. With this particular structural motif these compounds are ideally preorganized to form large macrocycles by the reaction with dicarboxylic acids. Indeed, heterocyclic compounds were formed in very selective reactions, which, depending on the rigidity of the backbone of the bridging ligands, had two or four Ga–Ga bonds in single molecules (**3**, Scheme 1) [8]. These compounds may be described as soluble, molecular analogues of metalorganic frame-work materials, which have been generated by the application of the same kind of ligands [9]. Surprisingly, also reactions in the presence of an excess of water did not result in the cleavage of the Ga–Ga bonds, instead molecular boxes with bridging hydroxo and carboxylato groups (**4**, Scheme 1) [10] or a novel subhydroxide of gallium [11] have been isolated.

We report herein on our first experiments to synthesize functionalized dicarboxylatodigallium compounds, which are potentially suitable to coordinate metal atoms or to form adducts by hydrogen bonding and may open the access to interesting supramolecular aggregates.

Results and Discussion

Reactions of the Digallium Compound 1 with Carboxylic Acids by Retention of the Ga–Ga Bonds

The tetraalkyldigallium compound **1** was treated with 14 different functionalized carboxylic acids having additional nitrogen, phosphorus, or oxygen donor atoms [Equation (1), Scheme 2]. The synthetic procedure followed the standard method already published in the literature [8]. THF was applied as a solvent because due to our experience it is the most effective solvent for these proton transfer reactions. The digallium compound **1** was dissolved in THF and added to a solution of the acid in the same solvent or treated with the solid acids at room temperature. The yellow color of **1** disappeared, and NMR spectroscopy revealed that the starting compounds were consumed completely after stirring of the mixtures for 12

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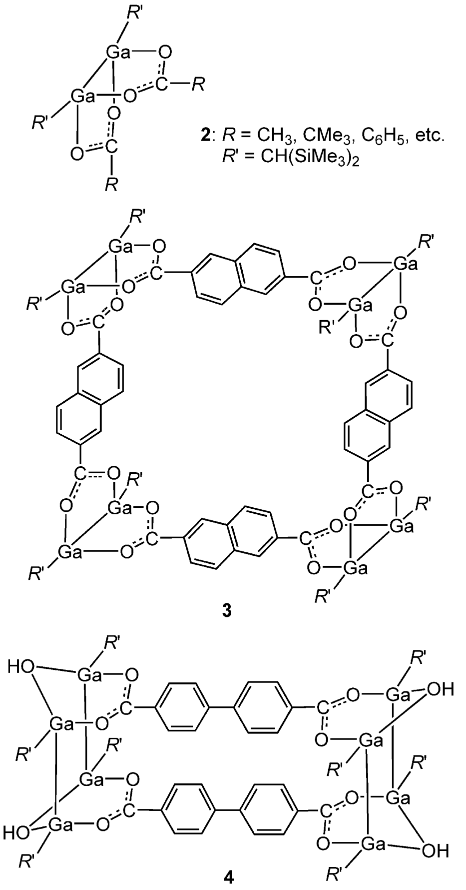
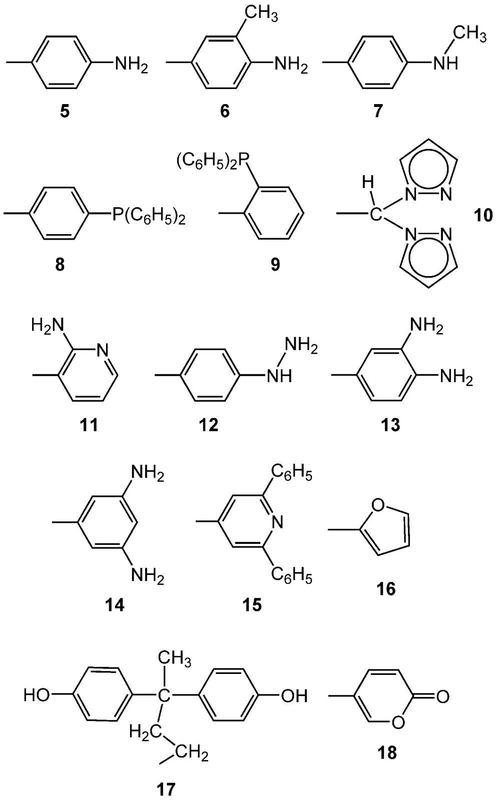


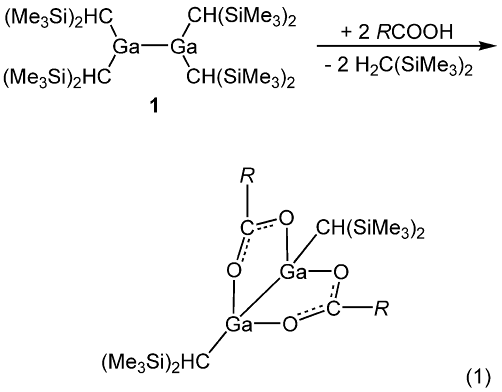
Scheme 1.



Scheme 2. Substituents *R* of the carboxylic acids applied in Equation (1).

to 48 hours. Many of these carboxylic acids are only sparingly soluble in THF. Suspensions resulted, and the completion of the reactions was indicated by the formation of clear solutions. Usually, these solutions were concentrated and cooled to get colorless solids of the products. In some cases relatively pure compounds were directly obtained by complete removal of all volatiles and washing of the remaining raw products with *n*-pentane. Only compound **8** was obtained as a highly viscous liquid, which could not be isolated in a solid form and could not be purified by recrystallization. However, its purity was high enough to allow its characterization and unambiguous identification by spectroscopic methods.

The ^{1}H NMR spectra of all products (**5** to **18**) exhibit the expected integration ratios with one bis(trimethylsilyl)methyl group per one carboxylato ligand in all cases. The resonances of the methine protons ($GaCHSi_2$) appear at about δ = –0.1 to –0.5. They are considerably shifted to a higher field compared to the corresponding value of the starting compound **1** (δ = 1.11) [2], which is essentially caused by the enhancement of the coordination number of the gallium atoms from three to four and has been observed several times before for mononuclear or dinuclear bis(trimethylsilyl)methylgallium compounds [12]. A similar alteration resulted for the chemical shifts of the carbon atoms attached to gallium (δ = 25.9 for **1** compared to about δ = 5 for the digalliumdicarboxylates **5** to **18**).



(1)

5 to **18**

Despite intensive efforts only few compounds (**9**, **10**, **15**, and **16**) could be obtained as single crystals suitable for crystal structure determinations. Three of these (**9**, **15** and **16**; Figure 1, Figure 2, and Figure 3) have the expected molecular structures, which have the intact Ga–Ga bonds symmetrically bridged by two chelating carboxylato ligands. The Ga–Ga bond lengths [237.49(4), 237.11(5), 237.48(av) pm] are in a very narrow range and correspond to standard values of those digallium dicarboxylates [7, 8, 10]. They are considerably shorter than the Ga–Ga distance in the tetraalkyldigallium starting compound **1** (254.1 pm), which is caused by the bridg-

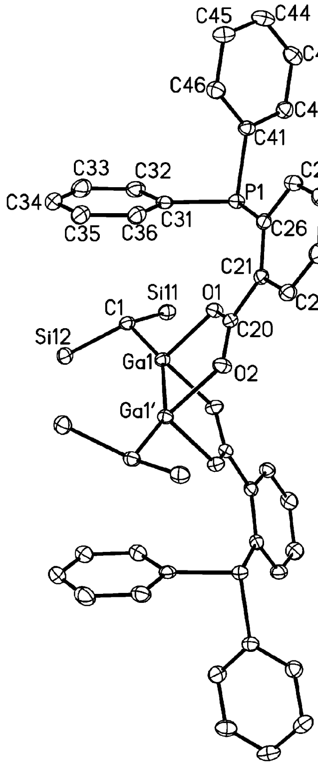


Figure 1. Molecular structure and numbering scheme of **9**; the thermal ellipsoids are drawn at the 40 % probability level; methyl groups and hydrogen atoms are omitted. Selected bond lengths /pm and angles /°: Ga1–Ga1' 237.49(4), Ga1–C1 195.7(2), Ga1–O1 202.2(1), Ga1–O2' 201.7(1), Ga1'–Ga1–C1 153.40(5), O1–Ga1–O2' 97.04(5), Ga1'–Ga1–O1 89.15(4), Ga1'–Ga1–O2' 87.12(4); Ga1' and O2' generated by *–x*, *y*, 0.5*–z*.

ing ligands and by the coordination of the gallium atoms to electronegative oxygen atoms. Also, the Ga–O [200.1(3) to 202.6(1) pm] and C–O distances of the carboxylato groups [126.5(2) to 128.3(4) pm] are in the expected ranges. The carboxylato groups adopt an almost ideal perpendicular arrangement with angles O–Ga–O between 93.9 and 97.0°. The largest angle belongs to the sterically most encumbered diphenylphosphanyl derivative **9**. The angles C–Ga–Ga including the central carbon atoms to the terminal alkyl groups approach linearity (153.4 to 159.0°). This particular situation at the Ga–Ga bonds of these molecules has been interpreted in terms of sp-hybridized gallium atoms [13]. The sp-orbitals are involved in the formation of the Ga–Ga bonds and the terminal Ga–C bonds, whereas the Ga–O interactions are essentially mediated by the remaining p orbitals. The diphenylisonicotinic carboxylato compound **15** shows an interesting arrangement of the molecules with strong intermolecular interactions in the solid state. The phenyl rings and the central pyridinyl group of one ligand are almost ideally in a plane with a maximum deviation of an atom from the mean plane of only 9 pm. The pyridyl and one phenyl ring of each ligand have close contacts to the pyridyl ring and a phenyl group of a neighboring molecule, as shown with three formula units of **15** in Figure 4. The average distance between the rings is about 350 pm indicating an interaction by π stacking [14]. One-dimensional coordination polymers result, which, caused by the perpendicular arrangement of the carboxylato ligands at the Ga–Ga bonds, form zigzag chains of the monomeric formula units. These secondary interactions influence considerably the solubility of **15**. Once crystallized it becomes insoluble in organic solvents such as *n*-pentane, toluene, 1,2-difluorobenzene, or even THF.

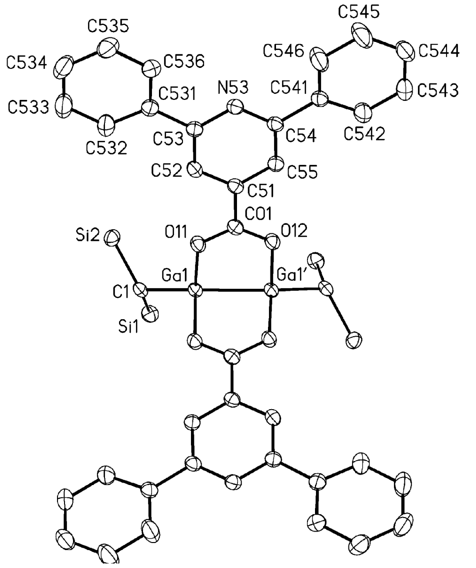


Figure 2. Molecular structure and numbering scheme of **15**; the thermal ellipsoids are drawn at the 40 % probability level; methyl groups and hydrogen atoms are omitted. Selected bond lengths /pm and angles /°: Ga1–Ga1' 237.11(5), Ga1–C1 195.1(2), Ga1–O11 202.6(1), Ga1–O12' 201.2(2), Ga1'–Ga1–C1 154.25(7), O11–Ga1–O12' 93.86(6), Ga1'–Ga1–O11 86.93(4), Ga1'–Ga1–O12' 89.65(4); Ga1' and O12' generated by *–x*, *y*, 0.5*–z*.

In contrast, compound **10** shows a completely different and unprecedented structural motif (Figure 5; schematic drawing in Scheme 3). It forms dimeric formula units, which possess two Ga–Ga bonds. Each Ga_2 couple is bridged by only one chelating carboxylato group with Ga–O (205.4 pm on average) and C–O bond lengths (125.2 pm) in narrow ranges as described before. The Ga–Ga bonds [239.44(8) pm] are only slightly lengthened compared to the twofold bridged species discussed above. The second type of carboxylato ligands coordinates only to a single gallium atom via one of the oxygen atoms. Expectedly the respective Ga–O distances [Ga1–O21 192.0(2) pm] are considerably shorter than those including the bridging carboxylato groups. Two different C–O distances result [127.5(4) and 120.6(5) pm] which indicate a more localized bonding situation including a terminal C=O double bond. The second gallium atom (Ga2) completes its coordination sphere by an interaction to a nitrogen atom of a pyrazolyl group [Ga2–N14' 219.2(3) pm] of a neighboring molecule. The Ga–N bond length is in the upper range characteristic of dative Ga–N interactions [15]. Two of these interactions give the dimeric formula unit of **10** in the solid state. The pyrazolyl groups involved in this adduct formation are part of those carboxylato groups which bridge the Ga–Ga bonds. The determination of the molar mass of **10** in benzene by cryoscopy clearly

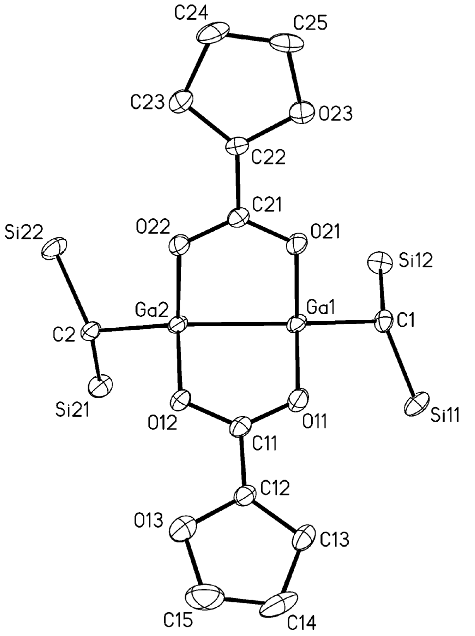


Figure 3. Molecular structure and numbering scheme of **16**; the thermal ellipsoids are drawn at the 40 % probability level; hydrogen atoms and methyl groups are omitted. Selected bond lengths /pm and angles /° (values of the second molecule in square brackets): Ga1–Ga2 237.68(6) [237.27(6)], Ga1–C1 195.9(4) [195.2(4)], Ga2–C2 195.3(4) [195.8(4)], Ga1–O11 200.9(3) [201.7(3)], Ga1–O21 202.3(2) [200.1(3)], Ga2–O12 202.4(2) [200.3(3)], Ga2–O22 200.5(3) [201.9(2)], Ga1–Ga2–C2 155.0(1) [155.1(1)], Ga2–Ga1–C1 159.0(1) [157.5(1)], O11–Ga1–O21 95.9(1) [96.3(1)], O12–Ga2–O22 95.0(1) [94.7(1)], Ga1–Ga2–O12 88.83(7) [88.84(8)], Ga1–Ga2–O22 88.82(8) [88.46(8)], Ga2–Ga1–O11 87.62(8) [87.77(7)], Ga2–Ga1–O21 87.76(8) [88.28(8)].

indicated the complete dissociation of the dimers to yield the monomeric molecular fragments. In accordance with results of mass spectrometric investigations also compound **11** seems to adopt a dimeric or oligomeric structure in the solid state.

Cleavage of the Ga–Ga Bonds

The reactions described so far proceeds selectively by the replacement of alkyl groups and retainment of the Ga–Ga bonds. Digallium compounds possessing functionalized carboxylato ligands became accessible on facile routes which are important starting materials for the generation of secondary products by, for instance, adduct formation. With the particular perpendicular arrangement of the carboxylato ligands they may open the access to the formation of macrocyclic or cage-like compounds and to supramolecular chemistry. However, these substituent exchange reactions are by no means trivial, and the additional donor atoms prevented the desired reaction courses in several cases. We observed cleavage of the Ga–Ga bonds by hydrogen release and oxidation of the gallium atoms when we treated the digallium compound **1** with particular functionalized carboxylic acids such as 3-aminopyrazine-2-carboxylic acid, 2,2-dithiosalicylic acid, dl-methionine, 1H-imidazole-4-carboxylic acid, or 1,2,4-triazole-3-carboxylic acid. Generally, monomeric mononuclear compounds were formed in which a GaR_2 fragment is coordinated by a chelating carboxylato ligand. We do not want to go into detail here. However, in one case a relatively interesting molecular structure resulted which is worth mentioning. When we treated compound **1** with isonicotinic acid we isolated colorless crystals of compound **19** in a moderate yield of 30 % [Equation (2)]. The ^{1}H NMR spectrum showed the resonances of the bis(trimethylsilyl)methyl groups and the carboxylato ligands in a molar ratio of 2:1, which is in accordance with the cleavage of the Ga–Ga bond. Chemical shifts are similar to those of the digallium species. The resonance of the methine protons close to gallium (δ = –0.28) may indicate a coordination number of four at the gallium atoms in solution.

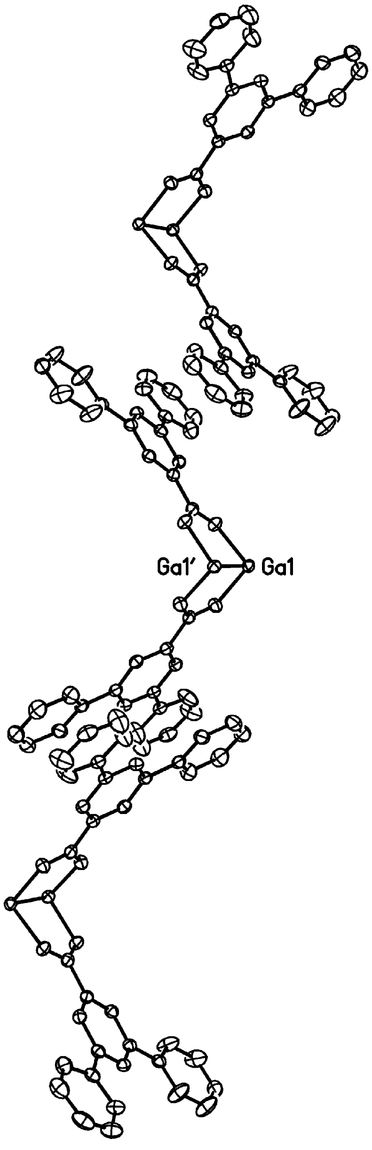


Figure 4. Part of the polymeric chain of **15**; bis(trimethylsilyl)methyl groups and hydrogen atoms are omitted.

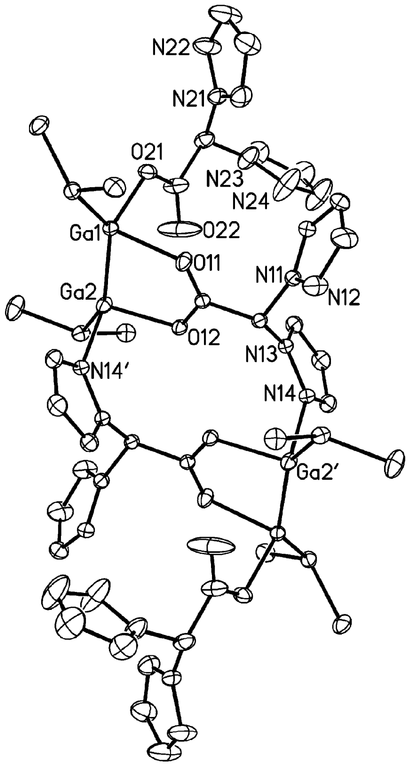
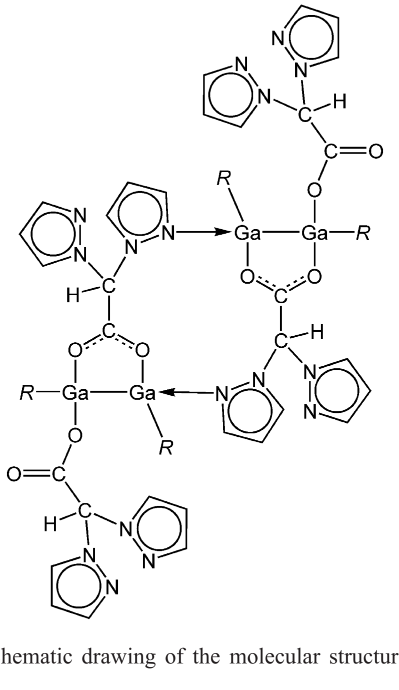
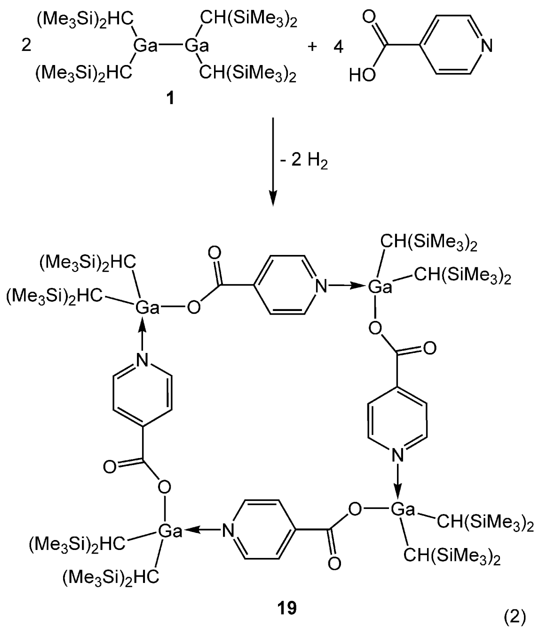


Figure 5. Molecular structure and numbering scheme of $(\mathbf{10})_2$; the thermal ellipsoids are drawn at the 40 % probability level; methyl groups and hydrogen atoms are omitted. Selected bond lengths /pm and angles /°: Ga1–Ga2 239.44(8), Ga1–C1 196.0(3), Ga2–C2 196.4(3), Ga1–O11 206.5(2), Ga1–O21 192.0(2), Ga2–O12 204.2(2), Ga2–N14' 219.2(3), Ga2–Ga1–C1 140.96(9), Ga1–Ga2–C2 148.23(9), O11–Ga1–O21 91.0(1), O12–Ga2–N14' 83.52(9), Ga2–Ga1–O11 85.41(6), Ga2–Ga1–O21 110.20(7), Ga1–Ga2–O12 90.13(6), Ga1–Ga2–N14' 99.72(7); N14' generated by –*x*+2, –*y*+1, –*z*+1.



Scheme 3. Schematic drawing of the molecular structure of **10** [R = $CH(SiMe_3)_2$].



(2)

Crystal structure determination of **19** revealed an interesting tetrameric compound in the solid state (Figure 6). It possesses a square molecular core in which four isolated gallium atoms (GaR_2 groups) are bridged by four isonicotinic carboxylato ligands. With this particular structural motif it resembles numerous tetrameric transition metal compounds reported in recent literature [16]. Each gallium atom is coordinated by two terminal alkyl groups, by a nitrogen atom of a pyridyl ring and an oxygen atom of a carboxylato group. The second oxygen atom is not involved in the coordination of the metal atom. The Ga–O (192.3 pm on average) and Ga–N distances (209.3 pm) are

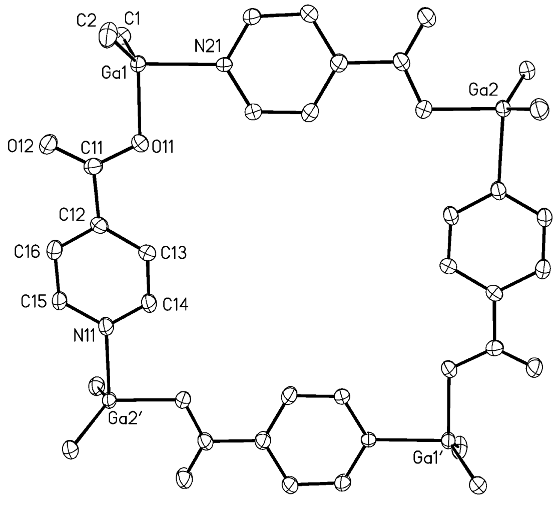


Figure 6. Molecular structure and numbering scheme of **19**; the thermal ellipsoids are drawn at the 40 % probability level; trimethylsilyl groups and hydrogen atoms are omitted. Selected bond lengths /pm and angles /°: Ga1–C1 198.0(4), Ga1–C2 198.2(4), Ga2–C3 198.0(4), Ga2–C4 198.3(4), Ga1–O11 192.2(6), Ga1–N21 208.5(7), Ga2–O21 192.4(5), Ga2–N11' 210.1(8), O11–Ga1–N21 89.3(2), O21–Ga2–N11' 88.7(2); Ga1', Ga2' and N11' generated by –*x*+1, –*y*+2, –z.

similar to or slightly shorter than those of the digallium compound **10** described above. The C–O bond lengths (129.3 and 121.3 pm) show the differences expected for a localized bonding situation in the CO_2 group. Owing to the molecular symmetry of **19** in the solid state the four gallium atoms are exactly in a plane. They form an ideal square with Ga–Ga separations along the edges of 892 pm and angles of 90°. The overall diameter of these molecules is at about 2.1 nm.

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane with $LiAlH_4$; toluene and THF over Na/benzophenone). The tetraalkyldigallium compound **1** was obtained according to a literature procedure [2]. Most acids are commercially available; they were dried in vacuo prior to use. Bis(pyrazol-1-yl)acetic acid was synthesized according to a procedure reported by *Burzlaff* [17]. Only the most intensive masses of a particular molecular fragment are given in the description of the mass spectra; the isotopic patterns are in agreement with the calculated ones.

Syntheses of Compounds 5 to 10; General Procedure

A solution of the digallium compound **1** (0.2 to 0.7 mmol) in THF (20 mL) was added to a solution of two equivalents of the respective carboxylic acid in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo. The residue was washed with *n*-pentane (**5** to **7**; **10**) or recrystallized from THF (**9**) to yield the colorless digalliumdicarboxylates in high purity. Compound **8** was soluble in *n*-pentane, but could not be crystallized.

Reaction with 4-Aminobenzoic Acid; Characterization of 5: Yield 49 %. M.p. (argon, sealed capillary): 145 °C (dec.). **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.18 (d, 4 H, $^3J_{H,H}$ = 8.1 Hz, *ortho*-H of phenyl), 6.04 (d, 4 H, $^3J_{H,H}$ = 8.1 Hz, *meta*-H of phenyl), 2.85 (s, 4 H, NH_2), 0.44 (s, 36 H, $SiMe_3$), –0.12 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 177.6 (CO_2), 151.8 (C–N), 133.1 (*ortho*-C of phenyl), 120.7 (*ipso*-C of phenyl), 113.7 (*meta*-C of phenyl), 4.3 (Ga–C), 3.6 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = 0.3. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3483 w, 3362 w, 3200 w νNH_2; 2957 vs, 2851 vs. (paraffin); 1919 vw, 1651 w, 1643 w, 1601 w, 1557 vw, 1514 vw δNH_2, νCO_2, phenyl; 1460 vs, 1375 vs. (paraffin); 1298 w, 1244 w δCH_3; 1205 w, 1171 m, 1152 w, 1051 vw νCC, νCN; 1011 w δCH; 964 w, 874 w, 843 m, 781 w ρCH_3(Si); 721 s (paraffin); 675 vw ν_{as}SiC; 633 w ν_sSiC; 546 vw, 501 vw, 461 vw νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 470 K): *m*/*z* (%) 728 (1), 730 (3), 732 (5) (M^+), 364 (10), 366 (7) (1/2 M^+).

Reaction with 4-Amino-3-methylbenzoic Acid; Characterization of 6: Yield 34 %. M.p. (argon, sealed capillary): 116 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.15 (d, 2 H, $^3J_{H,H}$ = 8.1 Hz, *ortho*-H of phenyl), 8.07 (s, 2 H, *ortho*-H of phenyl, C*H*–C–CH_3), 6.11 (d, 2 H, $^3J_{H,H}$ = 8.1 Hz, *meta*-H of phenyl), 2.96 (s, 4 H, NH_2), 1.63 (s, 6 H, CH_3 of phenyl), 0.46 (s, 36 H, $SiMe_3$), –0.07 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 177.8 (CO_2), 150.0 (C–N), 3.6 ($SiMe_3$), 134.0 (*ortho*-C of phenyl, *C*H–C–CH_3), 130.1 (*ortho*-CH of phenyl, *C*H–CH), 120.9 (*ipso*-C of phenyl), 120.7 (*meta*-C–CH_3 of phenyl), 113.7 (*meta*-CH of phenyl), 16.9 (CH_3 of phenyl), 4.3 (Ga–C). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = 0.2. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3487 w, 3395 m, 3213 vw νNH_2; 2924 vs, 2853 vs. (paraffin); 1684 w, 1653 w, br., 1558 w, 1521 w νCO_2, phenyl; 1458 vs, 1375 vs. (paraffin); 1304 m, 1246 m δCH_3; 1151 m, 1124 w νCC, νCN; 1018 w δCH; 966 w, 937 w, 916 vw, 872 m, 845 s, 781 m, 758 m ρCH_3(Si); 721 s (paraffin); 669 w ν_{as}SiC; 642 w, 624 w ν_sSiC; 548 w, 513 w, 463 w νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 410 K): *m*/*z* (%) 756 (0.7), 758 (1), 760 (0.5) (M^+), 597 (30), 599 (46), 601 (19) [M^+ – $CH(SiMe_3)_2$], 378 (58), 380 (45) (1/2 M^+).

Reaction with 4-Methylamino-benzoic Acid; Characterization of 7: Yield: 36 %. M.p. (argon, sealed capillary): 134 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.28 (d, 4 H, $^3J_{H,H}$ = 8.4 Hz, *ortho*-H of phenyl), 6.08 (d, 4 H, $^3J_{H,H}$ = 8.4 Hz, *meta*-H of phenyl), 2.93 (q, 2 H, $^3J_{H,H}$ = 4.8 Hz, NH), 2.05 (d, 6 H, $^3J_{H,H}$ = 4.8 Hz, N–CH_3), 0.48 (s, 36 H, $SiMe_3$), –0.10 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 177.8 (CO_2), 153.8 (C–N), 133.1 (*ortho*-C of phenyl), 119.6 (*ipso*-C of phenyl), 111.3 (*meta*-C of phenyl), 29.5 (N–CH_3), 4.3 (Ga–C), 3.7 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = 0.4. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3424 m νNH; 2949 vs, 2914 vs, 2847 vs. (paraffin); 1607 s, 1524 m νCO_2, phenyl; 1462 vs, 1377 vs. (paraffin); 1339 m, 1279 w, 1246 m δCH_3; 1180 s, 1157 w, 1105 w, 1063 w νCN, νCC; 964 w, 868 m, 841 vs, 781 m, 760 w ρCH_3(Si); 721 m (paraffin); 704 w, 677 w ν_{as}SiC; 644 w, 629 w ν_sSiC; 505 w, 436 w νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 300 K): *m*/*z* (%) 757 (8), 759 (13), 760 (6), 761 (6) (M^+ + H), 378 (16), 380 (12) (1/2 M^+).

Reaction with 4-Diphenylphosphino-benzoic Acid; Characterization of 8: A highly viscous liquid remained after removal of all volatile components. It could not be obtained as a solid. The raw product contained less than 5 % impurities which allowed an unequivocal spectroscopic characterization. **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.18 (d, 4 H, $^3J_{H,H}$ = 8.0 Hz, *ortho*-H of phenyl-CO_2), 7.29 (d, 4 H, $^3J_{H,H}$ = 8.0 Hz, *meta*-H of phenyl-CO_2), 7.29 (m, 8 H, *ortho*-H of PPh_2), 7.05 (m, 4 H, *para*-H of PPh_2), 7.04 (m, 8 H, *meta*-H of PPh_2), 0.37 (s, 36 H, $SiMe_3$), –0.17 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 174.4 (s, CO_2), 145.7 (d, $^1J_{C,P}$ = 16.0 Hz, *para*-C of phenyl–CO_2, C–P), 136.9 (d, $^1J_{C,P}$ = 11.8 Hz, *ipso*-C of PPh_2), 134.3 (d, $^2J_{C,P}$ = 20.3 Hz, *ortho*-C of PPh_2), 133.6 (d, $^2J_{C,P}$ = 20.3 Hz, *meta*-C of phenyl–CO_2), 131.3 (s, *C*–CO_2 of phenyl), 130.7 (d, $^3J_{C,P}$ = 6.4 Hz, *ortho*-C of phenyl–CO_2), 129.3 (s, *para*-C of PPh_2), 129.0 (d, $^3J_{C,P}$ = 7.4 Hz, *meta*-C of PPh_2), 5.0 (s, Ga–C), 3.7 (s, $SiMe_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = 0.2. **^{31}P NMR** (162 MHz, C_6D_6): δ = –4.6.

Reaction with 2-Diphenylphosphino-benzoic Acid; Characterization of 9: Yield 21 %. M.p. (argon, sealed capillary): 172 °C (dec.). **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.11 (m, 2 H, 6-H of phenyl-CO_2), 7.42 (2 H, *pseudo*-t, $^3J_{H,H}$ = 7.4 Hz, 5-H of phenyl-CO_2), 7.37 (2 H, *pseudo*-t, $^3J_{H,H}$ = 7.2 Hz, 4-H of phenyl–CO_2), 7.26 (m, 12 H, *meta*-H and *para*-H of PPh_2), 7.18 (m, 8 H, *ortho*-H of PPh_2), 6.88 (m, 2 H, 3-H of phenyl–CO_2), 0.10 (s, 36 H, $SiMe_3$), –0.47 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 178.4 (s, CO_2), 141.7 (d, $^1J_{C,P}$ = 29.2 Hz, 2-C of phenyl–CO_2), 139.9 (d, $^1J_{C,P}$ = 13.3 Hz, *ipso*-C of PPh_2), 136.8 (d, $^2J_{C,P}$ = 20.3 Hz, 1-C of phenyl–CO_2), 135.2 (s, 3-C of phenyl–CO_2), 134.7 (d, $^2J_{C,P}$ = 20.8 Hz, *ortho*-C of PPh_2), 133.2 (s, 4-C of phenyl–CO_2), 132.7 (s, br., 6-C of phenyl–CO_2), 129.3 (d, $^3J_{C,P}$ = 7.0 Hz, *meta*-C of PPh_2), 129.3 (s, *para*-C of PPh_2), 129.0 (s, 5-C of phenyl–CO_2), 4.5 (s, Ga–C), 3.4 (s, $SiMe_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = –0.4. **^{31}P NMR** (162 MHz, C_6D_6): δ = –3.9. **IR** (CsI, paraffin): $\tilde{\nu}$ = 1973 vw, 1956 w, 1888 w, 1803 vw, 1590 w, 1568 m, 1533 m phenyl, νCO_2; 1462 vs. (paraffin); 1447 s P-phenyl; 1377 vs. (paraffin); 1306 w, 1281 w, 1258 m, 1246 s δCH_3; 1180 w, 1153 m, 1117 vw, 1092 m, 1061 w νCC; 1016 s δCH; 999 m, 949 s, 912 vw, 841 vs, 775 vw, 756 m, 746 m ρCH_3(Si); 719 s (paraffin); 694 s ν_{as}SiC; 654 s, 627 w, 610 w ν_sSiC, νPC; 523 m, 509 s, 476 s νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 430 K): *m*/*z* (%) 1066 (0.7), 1068 (1), 1069 (0.5), 1070 (0.5) (M^+), 1051 (0.7), 1053 (1), 1054 (0.5), 1055 (0.5) ($M^+ - CH_3$), 907 (55), 909 (85), 910 (48), 911 (45) [$M^+ - CH(SiMe_3)_2$], 533 (57), 535 (45) (1/2 M^+).

Reaction with Bis(pyrazol-1-yl)acetic Acid; Characterization of 10: Yield 88 %. M.p. (argon, sealed capillary): 123 °C (dec.). **^{1}H NMR** (400 MHz, C_6D_6): δ = 7.55 (d, 4 H, $^3J_{H,H}$ = 1.6 Hz, 3-H of pyrazolyl), 7.44 (d, 4 H, $^3J_{H,H}$ = 2.4 Hz, 5-H of pyrazolyl), 7.15 (s, 2 H, $CHCO_2$), 5.98 (4 H, *pseudo*-t, $^3J_{H,H}$ = 2.2 Hz, 4-H of pyrazolyl), 0.13 (s, 36 H, $SiMe_3$), –0.47 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): δ = 177.1 (CO_2), 141.0 (3-C of pyrazolyl), 130.4 (5-C of pyrazolyl), 107.1 (4-C of pyrazolyl), 76.2 (*C*CO_2), 5.1 (Ga–C), 3.3 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6): δ = 0.0. **IR** (CsI, paraffin): $\tilde{\nu}$ = 1701 m, 1603 s, 1516 w νCO_2, pyrazolyl; 1456 vs. (paraffin); 1410 w δCH_3; 1377 s (paraffin); 1366 m, 1310 w, 1300 w, 1279 w, 1248 s δCH_3; 1190 w, 1175 vw, 1088 m, 1047 m νCC, νCN; 1011 w δCH; 961 w, 951 w, 917 w, 843 vs, 752 s ρCH_3(Si); 727 w (paraffin); 673 m ν_{as}SiC; 631 w, 609 vw ν_sSiC; 587 vw, 503 w, 438 vw νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 400 K): *m*/*z* (%) 838 (1.5), 840 (2.5), 841 (1.6), 842 (1.5) (M^+), 823 (2), 825 (3), 826 (1.5), 827 (1.5) ($M^+ - CH_3$), 679 (6), 681 (9), 682 (4), 683 (4) [$M^+ - CH(SiMe_3)_2$], 419 (100), 421 (77) (1/2 M^+).

Syntheses of Compounds 11 to 16; General Procedure

A solution of the digallium compound **1** (0.3 to 0.6 mmol) in THF [50 mL (20 mL in the case of **15** and **16**)] was treated with two equivalents of the solid carboxylic acids in small portions at room temperature. The suspensions were stirred at room temperature for 12 to 48 h until clear solutions resulted. The solutions were concentrated and cooled to +4 °C (**11**, **12**, and **16**) or –30 °C (**15**) to obtain colorless solids of the respective carboxylates. In the cases of the compounds **13** and **14**, all volatiles of the reaction mixtures were completely removed in vacuo, and the residues were washed with *n*-pentane to get colorless amorphous solids.

Reaction with 2-Aminonicotinic Acid; Characterization of 11: Yield 75 %. M.p. (argon, sealed capillary): 253 °C (dec.). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 8.19 (d, 2 H, $^3J_{H,H}$ = 7.7 Hz, *ortho*-C–H), 8.13 (d, 2 H, $^3J_{H,H}$ = 4.6 Hz, *para*-C–H), 6.92 (s, 4 H, NH_2), 6.53 (dd, 2 H, $^3J_{H,H}$ = 7.7 and 4.6 Hz, *meta*-C–H), 0.21 (s, 36 H, $SiMe_3$), –0.20 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D_8]THF): δ = 178.5 (CO_2), 161.2 (*ortho*-C–NH_2), 155.5 (*para*-C), 142.2 (*ortho*-C–H), 112.9 (*meta*-C), 107.3 (*ipso*-C), 5.0 (Ga–C), 3.6 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): δ = 0.0. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3630 w, 3499 w, 3422 m, 3366 m, 3277 w νN–H; 2924 vs, 2853 vs. (paraffin); 1674 s, 1618 s, 1595 s, 1578 s, 1558 s νCO_2, δNH_2; 1460 vs, 1375 vs. (paraffin); 1248 s δCH_3;1202 w; 1148 m, 1086 w νCC, νCN; 1015 m δCH; 970 w, 914 vw, 897 vw, 843 vs, 777 m ρCH_3(Si); 723 w (paraffin); 679 s ν_{as}SiC; 633 vw, 615 vw ν_sSiC; 583 w, 536 w, 515 w, 469 w νGaC, νGaO cm^{-1}. **MS** (EI, 70 eV, 400 K): *m*/*z* (%) 1458 (0.06), 1460 (0.12), 1462 (0.05), 1464 (0.02) ($2M^+ - 4$ H), 1298 (0.35), 1300 (0.43), 1302 (0.43), 1304 (0.16) [$2M^+ - 4H - CH(SiMe_3)_2$], 728 (2), 730 (3), 732 (2) ($M^+ - 2$ H), 569 (7), 571 (11), 365 (13), 367 (9) (1/2 M^+).

Reaction with 4-Hydrazinobenzoic Acid; Characterization of 12: Yield 82 %. M.p. (argon, sealed capillary): 170 °C (dec). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 7.89 (d, 4 H, $^3J_{H,H}$ = 8.9 Hz, *ortho*-C-H), 6.86 (s, 2 H, N*H*–NH_2), 6.72 (d, 4 H, $^3J_{H,H}$ = 8.9 Hz, *meta*-C–H), 3.90 (s, 4 H, br., NH_2), 0.20 (s, 36 H, $SiMe_3$), –0.37 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D_8]THF): δ = 177.9 (CO_2), 157.6 (*para*-C), 133.2 (*ortho*-C), 119.5 (*ipso*-C), 110.5 (*meta*-C), 4.3 (Ga–C), 3.6 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): δ = 0.2. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3318 s, 3289 s, 3252 s, 3205 m, 3125 w νNH; 2927 vs, 2866 vs. (paraffin); 1915 w, 1689 w, 1603 vs, 1564 m, 1541 vw, 1520 w, 1497 m δNH_2, νCO_2, phenyl; 1462 vs, 1377 vs. (paraffin); 1350 vs, 1302 w, 1246 vs. δCH_3; 1179 vs, 1136 sh, 1103 m, 1057 w νCC, νCN; 1015 vs. δCH; 947 vs, 843 vs, 783 s, 756 m ρCH_3(Si); 727 m (paraffin); 705 vw, 671 m ν_{as}SiC; 646 m, 625 m ν_sSiC; 586 vw, 552 vw, 513 m, 498 m, 465 vw, 432 m νGaC, νGaO cm^{-1}. **MS** (EI, 70 eV, 473 K): *m*/*z* (%) 758 (0.7), 760 (1), 762 (0.5) (M^+), 743 (0.7), 745 (1), 747 (0.5) ($M^+ - CH_3$), 599 (29), 601 (40), 603 (17) [$M^+ - CH(SiMe_3)_2$], 379 (93), 381 (70) (1/2 M^+).

Reaction with 3,4-Diaminobenzoic Acid; Characterization of 13: Yield 65 %. M.p. (argon, sealed capillary): 155 °C (dec.). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 7.40 [2 H, dd, $^3J_{H,H}$ = 8.5 and 1.6 Hz, *ortho*-C(*H*)–C–H], 7.33 [2 H, s, $^3J_{H,H}$ = 1.6 Hz, *ortho*-C(*H*)–C–NH_2], 6.49 (d, 2 H, $^3J_{H,H}$ = 8.5 Hz, *meta*-C–H), 3.94 and 4.68 (each 4 H, s, br., NH_2), 0.19 (s, 36 H, $SiMe_3$), –0.36 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D_8]THF): δ = 178.4 (CO_2), 142.9 (*para*-C), 134.5 (*meta*-C–NH_2), 124.1 (*ortho*-C), 120.8 (*ipso*-C), 118.5 (*ortho*-C), 113.9 (*meta*-C–H), 4.2 (Ga–C), 3.7 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): δ = 0.1. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3437 m, 3375 m, 3197 w νNH; 2924 vs, 2853 vs. (paraffin); 1927 w, 1871 w, 1771 w, 1626 m, br. δN–H, νCO_2, phenyl; 1462 vs, 1375 vs. (paraffin); 1302 w, 1244 m δCH_3; 1152 m, 1070 m, 1051 m νCC, νCN; 1015 m δCH; 966 w, 841 s, br., 773 m ρCH_3(Si); 723 m (paraffin); 673 vw ν_{as}SiC; 648 vw, 613 vw ν_sSiC; 556 vw, 513 w, 449 m νGaC, νGaO cm^{-1}.

Reaction with 3,5-Diaminobenzoic Acid; Characterization of 14: Yield 79 %. M.p. (argon, sealed capillary): 181 °C (dec.). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 6.66 (s, 4 H, *ortho*-C-H), 6.04 (s, 2 H, *para*-C–H), 4.28 (s, 8 H, NH_2), 0.19 (s, 36 H, $SiMe_3$), –0.32 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D_8]THF): δ = 179.0 (CO_2), 149.9 (*meta*-C), 133.3 (*ipso*-C), 106.9 (*ortho*-C), 105.8 (*para*-C), 4.6 (Ga–C), 3.6 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): δ = 0.1. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3445 m, 3360 m, 3210 w νN–H; 2951 vs, 2851 vs. (paraffin); 1927 vw, 1856 vw, 1630 vs, br., 1533 m νCO_2, δNH_2, phenyl; 1456 vs, 1375 vs. (paraffin); 1341 sh, 1306 s, 1244 s δCH_3; 1188 m, 1090 w, 1049 m νCC, νCN; 1015 s δCH; 955 m, 869 s, 844 s, 770 m, 754 m ρCH_3(Si); 723 s (paraffin); 669 m ν_{as}SiC; 623 w, 613 w ν_sSiC; 565 w, 515 m, 465 m νGaC, νGaO cm^{-1}. **MS** (EI, 70 eV, 300 K): *m*/*z* (%) 379 (93), 381 (42) (1/2 M^+).

Reaction with 2,6-Diphenylisonicotinic Acid; Characterization of 15: Yield 64 %. M.p. (argon, sealed capillary): 195 °C (dec.). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 8.40 (s, 4 H, *ortho*-H of pyridyl), 8.21 (m, 8 H, *ortho*-H of phenyl), 7.49 (m, 8 H, *meta*-H of phenyl), 7.42 (m, 4 H, *para*-H of phenyl), 0.33 (s, 36 H, $SiMe_3$), –0.09 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D_8]THF): δ = 177.0 (CO_2), 158.7 (*meta*-C of pyridyl), 141.5 (*ipso*-C of pyridyl), 139.6 (*ipso*-C of phenyl), 130.3 (*para*-C of phenyl), 129.5 (*meta*-C of phenyl), 127.7 (*ortho*-C of phenyl), 118.8 (*ortho*-C of pyridyl), 5.7 (Ga–C), 3.7 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): δ = 0.6. **IR** (CsI, paraffin): $\tilde{\nu}$ = 1653 w, 1599 w, 1580 w, 1535 s, 1512 sh νCO_2, pyridyl; 1462 vs. (paraffin); 1418 m δCH_3; 1377 s (paraffin); 1317 m, 1244 m δCH_3; 1182 w, 1153 vw, 1117 vw, 1072 w, 1055 w νCC; 1016 s δCH; 932 m, 896 w, 845 s, 827 s, 764 s, 750 m ρCH_3(Si); 723 m (paraffin); 687 m, 673 w ν_{as}SiC; 652 w, 627 w, 613 w ν_sSiC; 536 w, 517 w, 503 m, 462 w νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 490 K): *m*/*z* (%) 1005 (8), 1007 (13), 1008 (8), 1009 (8) (M^+ + H), 845 (30), 847 (48), 848 (25), 849 (25) [$M^+ - CH(SiMe_3)_2$], 502 (83), 504 (64) (1/2 M^+).

Reaction with 2-Furoic Acid (furan-2-carboxylic acid); Characterization of 16: Yield 80 %. M.p. (argon, sealed capillary): 121 °C (dec.). **^{1}H NMR** (400 MHz, [D_8]THF): δ = 7.74 (s, 2 H, OCH), 7.25 (d, 2 H, $^3J_{H,H}$ = 3.5 Hz, OCHCHC*H*), 6.55 (m, 2 H, OCHC*H*), 0.19

(s, 36 H, SiMe$_3$), –0.29 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D$_8$]THF): δ = 169.4 (CO$_2$), 148.6 (OCH), 120.5 (OCHCHC*H*), 112.9 (OCHC*H*), 5.0 (Ga–C), 3.4 (SiMe$_3$). **^{29}Si NMR** (79.5 MHz, [D$_8$]THF): δ = 0.3. **IR** (CsI, paraffin): $\tilde{\nu}$ = 1925 w, 1871 w, 1856 w, 1798 w, 1778 w, 1740 w, 1701 vw, 1659 w, 1584 vs, 1535 m νCO$_2$, νCC, νCO; 1464 vs, 1375 s (paraffin); 1296 w, 1244 vs, 1231 sh δCH$_3$; 1200 s, 1139 s, 1078 m νCC; 1015 vs. δCH; 934 s, 883 m, 866 m, 845 vs, 758 m ρCH$_3$(Si); 723 m (paraffin); 673 s ν_{as}SiC; 613 s ν_sSiC; 594 m, 573 vw, 515 vs. νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 360 K): *m/z* (%) 678 (1), 680 (2), 682 (1) (M$^+$), 519 (33), 521 (49), 523 (19) [M$^+$ – CH(SiMe$_3$)$_2$], 339 (100), 341 (75) (1/2 M$^+$).

Syntheses of Compounds 17 and 18; General Procedure

The digallium compound **1** (0.3 mmol) and two equivalents of the carboxylic acids were suspended in THF (20 mL) at room temperature. The suspensions were stirred at room temperature for 16 h until clear solutions resulted. All volatiles were completely removed in vacuo, and the residues were washed with *n*-pentane to get colorless amorphous solids.

Reaction with 4,4-Bis(4-hydroxyphenyl)valeric Acid; Characterization of 17: Yield 66 %. M.p. (argon, sealed capillary): 181 °C (dec.). **^{1}H NMR** (400 MHz, [D$_8$]THF): δ = 7.94 (s, 4 H, OH), 6.95 (d, 8 H, $^3J_{H,H}$ = 8.5 Hz, *ortho*-H of phenyl), 6.59 (d, 8 H, $^3J_{H,H}$ = 8.5 Hz, *meta*-H of phenyl), 2.37 (m, 4 H, H$_3$C–C–C*H*$_2$–CH$_2$), 2.12 (m, 4 H, H$_3$C–C–CH$_2$–C*H*$_2$), 1.47 (s, 6 H, *H*$_3$C–C–CH$_2$–CH$_2$), 0.12 (s, 36 H, SiMe$_3$), –0.46 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D$_8$]THF): δ = 187.5 (CO$_2$), 156.5 (*para*-C of phenyl), 140.6 (*ipso*-C of phenyl), 128.9 (*ortho*-C of phenyl), 115.4 (*meta*-C of phenyl), 45.2 (H$_3$C–*C*–CH$_2$–CH$_2$), 38.4 (H$_3$C–C–*C*H$_2$–CH$_2$), 33.4 (H$_3$C–C–CH$_2$–*C*H$_2$), 28.2 (H$_3$*C*–C–CH$_2$–CH$_2$), 4.5 (Ga–C), 3.5 (SiMe$_3$). **^{29}Si NMR** (79.5 MHz, [D$_8$]THF): δ = 0.1. **IR** (CsI, paraffin): $\tilde{\nu}$ = 3406 w, br., 3175 w, br. νOH; 2947 vs, 2843 vs. (paraffin); 1703 w, 1645 m, 1611 m, 1591 m, 1557 m, 1502 sh νCO$_2$, phenyl; 1463 vs, 1377 vs. (paraffin); 1304 m, 1266 w, 1248 m δCH$_3$; 1169 s, 1155 m, 1082 w, 1049 w νCC, νCO; 1013 m δCH; 972 m, 918 w, 889 m, 866 m, 845 s, 762 s ρCH$_3$(Si); 723 m (paraffin); 679 w ν_{as}SiC; 635 vw ν_sSiC; 579 m, 559 m, 513 w, 485 w νGaC, νGaO cm^{-1}.

Reaction with Coumalic Acid (2-oxo-2H-pyran-5-carboxylic acid); Characterization of 18: Yield 79 %. M.p. (argon, sealed capillary): 132 °C (dec.). **^{1}H NMR** (400 MHz, [D$_8$]THF): δ = 8.39 (s, 2 H, OCH), 7.71 (d, 2 H, $^3J_{H,H}$ = 9.8 Hz, C*H*=CH–C=O), 6.29 (d, 2 H, $^3J_{H,H}$ = 9.8 Hz, CH=C*H*–C=O), 0.18 (s, 36 H, SiMe$_3$), –0.28 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, [D$_8$]THF): δ = 175.3 (CO$_2$), 161.4 (H–C–O), 159.3 (C=C–*C*=O), 141.9 (*C*=C–C=O), 115.5 (C=*C*–C=O), 113.3 (*C*–CO$_2$), 5.3 (Ga–C), 3.5 (SiMe$_3$). **^{29}Si NMR** (79.5 MHz, [D$_8$]THF): δ = 0.3. **IR** (CsI, paraffin): $\tilde{\nu}$ = 1755 vs. νC=O; 1713 s, 1639 s, 1564 m, 1533 m νCO$_2$, νC=C; 1462 vs, 1377 vs. (paraffin); 1306 m, 1246 s δCH$_3$; 1155 m, 1125 m, 1090 s, 1040 m νCC, νCO; 1015 s δCH; 943 s, 841 vs, 758 m ρCH$_3$(Si); 721 s (paraffin); 675 m ν_{as}SiC; 648 m, 620 w ν_sSiC; 557 w, 519 w, 484 m, 438 w νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 390 K): *m/z* (%) 734 (4), 736 (7), 738 (3) (M$^+$), 575 (59), 577 (85), 579 (37) [M$^+$ – CH(SiMe$_3$)$_2$], 367 (100), 369 (77) (1/2 M$^+$).

Table 1. Crystal data and structure refinement for compounds **9**, **10**, **15**, **16**, and **19**.

	9	**10**	**15**	**16**	**19**
Formula	$C_{60}H_{82}Ga_2O_6P_2Si_4$	$C_{74}H_{120}Ga_4N_{16}O_8Si_8$	$C_{50}H_{62}Ga_2N_2O_4Si_4$	$C_{24}H_{44}Ga_2O_6Si_4$	$C_{112}H_{232}Ga_4N_4O_{16}Si_{16}$
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group [18]	*C*2/*c*; No. 15	$P\bar{1}$; No. 1	*C*2/*c*; No. 15	$P\bar{1}$; No. 2	$P\bar{1}$; No. 2
Z	4	1	4	4	1
T /K	153(2)	153(2)	153(2)	153(2)	153(2)
Density (calc) / g·cm^{-3}	1.297	1.284	1.313	1.315	1.161
a /pm	3442.4(2)	1228.0(3)	2659.1(2)	980.1(1)	1468.30(8)
b /pm	870.80(6)	1437.8(4)	855.48(5)	1223.4(2)	1662.35(9)
c /pm	2657.3(3)	1609.6(5)	2551.2(2)	2992.2(4)	1798.7(1)
α /°	90	67.326(5)	90	93.172(2)	64.336(1)
β /°	128.752(1)	67.681(5)	120.022(2)	99.343(2)	77.526(1)
γ /°	90	86.671(5)	90	102.783(2)	71.940(1)
V /nm^3	6.2121(9)	2.4128(12)	5.0928(5)	3.467(8)	3.7452(4)
μ /mm^{-1}	1.043	1.259	1.196	1.739	0.892
Crystal size /mm	0.17 × 0.13 × 0.05	0.12 × 0.05 × 0.04	0.09 × 0.06 × 0.04	0.12 × 0.08 × 0.02	0.16 × 0.13 × 0.08
Radiation	Mo-K_α, graphite-monochromator				
Θ range for data collection /°	$1.52 \le \theta \le 27.92$	$1.49 \le \theta \le 30.04$	$1.75 \le \theta \le 27.51$	$1.39 \le \theta \le 31.59$	$1.26 \le \theta \le 27.54$
Index ranges	$-45 \le h \le 45, -11 \le k \le 11, -34 \le l \le 34$	$-17 \le h \le 17, -20 \le k \le 20, -22 \le l \le 22$	$-34 \le h \le 34, -11 \le k \le 11, -33 \le l \le 33$	$-13 \le h \le 14, -17 \le k \le 17, -43 \le l \le 44$	$-19 \le h \le 19, -21 \le k \le 21, -23 \le l \le 23$
Independent reflections	7425 (R_{int} = 0.0331)	13877 (R_{int} = 0.0317)	5842 (R_{int} = 0.0454)	21140 (R_{int} = 0.0515)	17170 (R_{int} = 0.0379)
Reflections $I > 2\sigma(I)$	6096	10156	4260	11731	11911
Parameters	340	469	286	673	772
R $[I > 2\sigma(I)]$	0.0316	0.0590	0.0345	0.0612	0.0652
wR_2 (all data)	0.0818	0.1662	0.0853	0.1537	0.2137
Max./min. residual electron density /10^{30}·em^{-3}	+597/–462	+1855$^{a)}$/–2649	+572/–256	+1354$^{a)}$/–1246	+1327$^{b)}$/–1026

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$

a) Close to gallium. b) Close to THF.

Reaction with Isonicotinic Acid; Synthesis of 19: A solution of the tetraalkyldigallium compound **1** (0.395 g, 0.51 mmol) in THF (50 mL) was treated with solid isonicotinic acid (0.125 g, 1.02 mmol) in small portions at room temperature. The suspension was stirred overnight. A clear, yellow solution resulted, which was concentrated and cooled to +4 °C to yield colorless crystals of the cleavage product **19**. Yield 0.157 g (30 %); M.p. (argon, sealed capillary): 153 °C (dec.). **^{1}H NMR** (400 MHz, C_6D_6): $\delta = 8.50$ (dd, 2 H, $^3J_{H,H} = 4.3$, $^4J_{H,H} = 1.6$ Hz, *meta*-C–H), 7.61 (dd, 2 H, $^3J_{H,H} = 4.3$, $^4J_{H,H} = 1.6$ Hz, *ortho*-C–H), 0.23 (s, 36 H, $SiMe_3$), –0.28 (s, 2 H, Ga–CH). **^{13}C NMR** (100 MHz, C_6D_6): $\delta = 180.1$ (CO_2), 151.4 (*meta*-C), 136.3 (*ipso*-C), 123.0 (*ortho*-C), 11.0 (Ga–C), 3.6 ($SiMe_3$). **^{29}Si NMR** (79.5 MHz, [D_8]THF): $\delta = -0.5$. **IR** (CsI, paraffin): $\tilde{\nu} = 1921$ w, 1865 w, 1663 vs, 1620 m, 1562 s, 1564 s, 1502 m νCO_2, pyridyl; 1464 vs, 1377 vs. (paraffin); 1242 vs. δCH_3; 1213 m, 1144 s, 1061 m, 1030 s νCC; 1015 vs. δCH; 968 vs, 843 vs, 773 m, 756 m ρCH_3(Si); 725 m (paraffin); 704 w, 667 m ν_{as}SiC; 627 m, 610 w ν_sSiC; 573 m, 498 s, 471 w, 446 m νGaC, νGaO cm^{-1}. **MS** (EI, 20 eV, 390 K): *m/z* (%) 494 (63), 496 (53) (M^+ of the monomer – CH_3), 350 (100), 352 (76) [M^+ of the monomer – $CH(SiMe_3)_2$].

Crystal Structure Determinations

Single crystals were obtained directly from the reaction mixtures (**9**, **15**, **16**, and **19**) or by recrystallization from toluene (**10**). The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1. The structures were solved by direct methods and refined with the program system SHELXL-97 [19] with full-matrix and all independent structure factors (F^2). All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}$(C). The molecules of **9** and **15** reside on twofold rotational axes. Compound **9** crystallizes with two molecules of THF per formula unit. They are located close to the diphenylphosphino ligands and are parallel to a phenyl group. The dimeric molecules of **10** are located on crystallographic centers of symmetry. Two toluene molecules are enclosed which are disordered with two different positions for the methyl groups. Compound **16** crystallizes with two independent molecules in the asymmetric unit. Compound **19** is tetrameric in the solid state. The molecules reside on crystallographic centers of symmetry. The bridging ligands are disordered over two positions. Their atoms were refined on split positions (0.76:0.24). The unit cell contains eight molecules of THF, which were refined with isotropic displacement parameters.

The crystallographic data were deposited as supplementary publication no. CCDC-752592 (**9**), -752589 (**10**), -752590 (**15**), -752591 (**16**), and -752592 (**19**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, Great Britain (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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