The Formation of Macrocyclic Compounds Containing Two Ga–Ga Bonds by the Reaction of Tetraalkyldigallane(4) $R_2Ga–GaR_2$ [R = $CH(SiMe_3)_2$] with Dicarboxylic Acids

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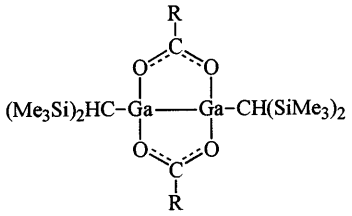
Tetrakis[bis(trimethylsilyl)methyl]digallane(4) **1** reacts with dicarboxylic acids like 1,4-benzenedi(methylcarboxylic) acid, 1,4-cyclohexanedicarboxylic acid, 1,6-hexanedicarboxylic acid, and 1,4-butanedicarboxylic acid (adipinic acid) by the release of two equivalents of bis(trimethylsilyl)methane and the retention of the Ga–Ga bond. Products are formed, in which the very short Ga–Ga bonds (237.7 pm on average) are bridged by two carboxylato groups. Two of these moieties are connected in each compound by two spacers (dimethylbenzene, cyclohexane, hexane, or butane) to form macrocyclic compounds with up to 22 atoms in the resultant heteroatomic rings. The dimeric form is also observed in solution. For comparison, the synthesis and structure of the product of the reaction of **1** with 1-adamantanecarboxylic acid is included, which also has the Ga–Ga bond (239.1 pm) bridged by two carboxylato groups.

Recently we published the reactions of tetrakis[bis(trimethylsilyl)methyl]digallane(4) **1**[1] with aromatic carboxylic acids. Remarkably, these reactions did not lead to the expected cleavage of the Ga−Ga bond of **1** as observed for the corresponding dialuminium or diindium derivatives[2], but two alkyl substituents were replaced by two carboxylato groups, and two equivalents of bis(trimethylsilyl)methane were released in an almost quantitative yield[3]. As shown in Scheme 1, the bidentate carboxylato ligands of the products occupy bridging positions across the Ga−Ga bond, which is significantly shortened to 238.5(2) pm compared with that of the starting compound **1** [254.1(1) pm][1]. In contrast, a terminal coordination of chelating diphenyltriazenido ligands was observed in a digallium compound obtained by the reaction of **1** with diphenyltriazene[4]. Also, the product of the reaction with dibenzoylmethane showed a terminal arrangement of the chelating groups[5], which have, however, two atoms more in the resulting heterocycle. The reason for the different coordination is not well understood; it may depend on the distance between the coordinating atoms (bite), and we hope to clarify this problem by the synthesis of some derivatives by systematically changing the size of the chelating groups. In this context, we report here on the structural characterization of the first example of a digallium compound with aliphatic carboxylato ligands in order to exclude an electronic influence of the aromatic groups on the coordination mode.

The reactions of **1** with carboxylic acids yielded the products almost quantitatively without any NMR spectroscopically detectable by-products[3]. Therefore, we were interested in the behavior of bifunctional dicarboxylic acids, which could give two different products: (i) The dicarboxylato ligand might be bound to only one digallium fragment in a chelating manner. But from molecular models it can be deduced that such an intramolecular coordination is not easy to achieve and requires long carbon chains to avoid considerable steric stress in the molecule. (ii) The dicarboxylato ligands could bridge two digallium units by an intermolecular coordination to form dimeric or oligomeric species. The oligomerization of the products would open an easy route to the synthesis of interesting new macrocyclic compounds. The reactions of some dicarboxylic acids with **1** and the complete characterization of the products is described in this article.

Scheme 1



R = -4-Br-C_6H_4

Reaction of Digallane(4) 1 with 1-Adamantanecarboxylic Acid

Two equivalents of 1-adamantanecarboxylic acid reacted rapidly with **1** in *n*-pentane at low temperature, and the yellow color of the digallium(4) compound disappeared already at −15°C. As shown by a NMR spectrum of the reac-

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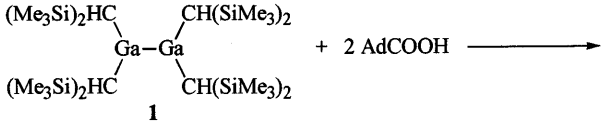
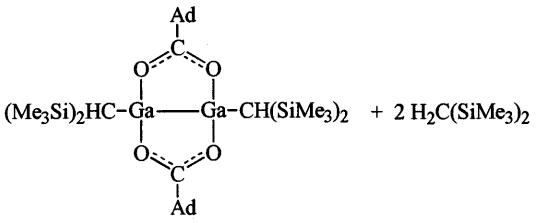
tion mixture, exactly two equivalents of bis(trimethylsilyl)-methane were released per formula unit of **1** (Eq. 1). The colorless, crystalline product (**2**) was isolated after evaporation and recrystallization from pentane in a yield of 79%. Product **2** is readily soluble in hydrocarbons. It is a monomer in benzene solution, as shown by the cryoscopical molar mass determination. The NMR resonances of the methine hydrogen and carbon atoms of the $CH(SiMe_3)_2$ substituents bound to gallium (^1H: $\delta = -0.30$; ^{13}C: $\delta = 4.0$) show a significant high-field shift relative to those of the starting compound **1** (^1H: $\delta = 1.11$; ^{13}C: $\delta = 25.9$[1]), which is very characteristic of an enhancement of the coordination number of the Ga atoms from 3 to 4[3][4][5][6]. The stretching vibration of the CO_2 group with a delocalized electronic π bond is observed in the IR spectrum at 1530 cm^{-1}.



1



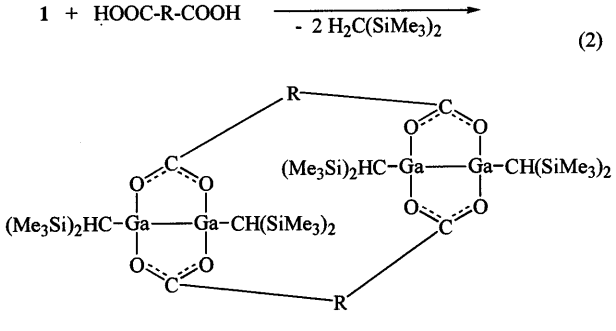
(1)

2 (Ad = adamantyl)

Reactions of 1 with Dicarboxylic Acids

The reactions of dicarboxylic acids with **1** were much slower than those with the monocarboxylic acids and required reaction times of several days in *n*-pentane at room temperature or some hours in boiling solvents. While, as expected, two equivalents of bis(trimethylsilyl)methane with respect to **1** were released in all reactions, only four acids reacted successfully to gave isolable products in high purity (Eq. 2): 1,4-benzenedi(methylcarboxylic) acid (product **3**), 1,4-cyclohexanedicarboxylic acid (product **4**), 1,6-hexanedicarboxylic acid (product **5**), and 1,4-butanedicarboxylic acid (adipinic acid) (product **6**). In contrast, other acids like maleic acid, 1,2- and 1,4-benzenedicarboxylic acid, 4,4′-oxydibenzoic acid and 2,2-dimethylpropane-1,3-dicarboxylic acid (glutaric acid) yielded only oily residues with mixtures of many unknown products, from which no compound could be isolated in a pure form. The products **3** to **6** were isolated after recrystallization in excellent yields of more than 80%.

The spectroscopic properties of the compounds **3** to **6** are very similar to those described above for **2** with the monocarboxylato ligand. The NMR resonances of the methine groups bound to gallium are shifted to high field (^1H: $\delta = -0.31$ to -0.47; ^{13}C: $\delta = 4.2$ to 4.5) relative to those of digallane(4) **1**, as expected for the enhancement of the coordination number at the Ga atoms to 4. The integration of



3: R = 1,4-$(CH_2)_2C_6H_4$
4: R = 1,4-C_6H_{10}
5: R = $(CH_2)_6$
6: R = $(CH_2)_4$

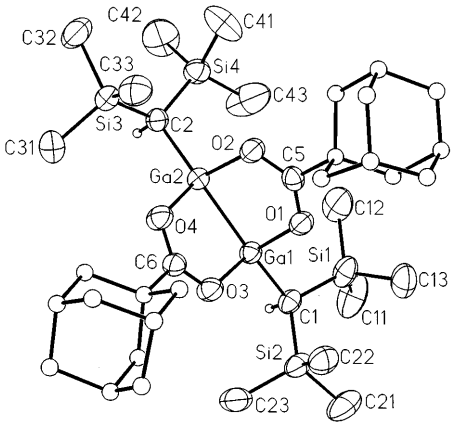
the ^1H-NMR spectra clearly reveals one dicarboxylato ligand each Ga_2R_2 formula unit. In the IR spectra of **3** to **6**, the most characteristic absorptions are those of the CO_2 stretching vibrations in a quite narrow range between 1539 and 1549 cm^{-1}. All products are dimeric in benzene solution as shown by the cryoscopical molar mass determination, so that compounds were formed, which contain two Ga_2R_2 moieties bridged by two dicarboxylato bridges.

Crystal Structures of 2, 3, and 4

The molecular structure of compound **2** is depicted in Figure 1. It is quite similar to the structure of the recently published *p*-bromobenzoate derivative[3] and has the Ga−Ga bond bridged by two adamantyl carboxylato groups. The Ga−Ga bond [239.1(1) pm] is shorter than that of the tetraalkyl compound **1** [254.1(1) pm][1], which may be caused by the carboxylato bridges with a short distance between the coordinating atoms of 223.2 pm on average. Both Ga−Ga distances lie within the broad range of known bond lengths between Ga atoms[7]. Two five-membered heterocycles are formed by the chelating coordination of the Ga−Ga bond, which are almost ideally planar and show a maximum deviation of an atom from the plane of 1.8 and 2.5 pm. Remarkably, these heterocycles arrange perpendicular to one another, and the angle between both chelating groups is 89.3°. The C−Ga−Ga−C center of the molecule is almost linear with large mean C−Ga−Ga angles of 158.7°. Thus, the coordination of the carboxylato groups seems to be based mainly on an interaction with two p orbitals of each Ga atom.

Compounds **3** and **4** contain macrocycles (Figures 2 and 3), and two digallium dicarboxylato units are bridged by hydrocarbon groups. The structure around the Ga−Ga bond of both molecules **3** and **4** is quite similar to that observed in compound **2**. Each Ga−Ga bond is bridged by two carboxylato groups, which results in short Ga−Ga bond lengths of 237.85 pm on average (**3**) and 237.46(4) pm (**4**). The C−Ga−Ga−C moieties are almost linear with C−Ga−Ga angles of 156.6° (**3**) and 155.8° (**4**). As in **2**, the Ga_2O_2C heterocycles are perpendicular to each other, and

Figure 1. Molecular structure and numbering scheme of compound **2**; the thermal ellipsoids are drawn at the 40% probability level; the carbon atoms of one of the disordered adamantyl groups are drawn with an arbitrary radius[a]



[a] Selected bond lengths [pm] and angles [°]: Ga1−Ga2 239.1(1), Ga1−O1 200.2(2), Ga1−O3 200.4(2), Ga1−C1 195.4(3), Ga2−O2 200.6(2), Ga2−O4 201.6(2), Ga2−C2 195.8(3), O1−Ga1−O3 91.1(1), O2−Ga2−O4 91.5(1), Ga2−Ga1−O1 87.67(8), Ga2−Ga1−O3 88.16(8), Ga1−Ga2−O2 87.80(8), Ga1−Ga2−O4 87.25(8), Ga2−Ga1−C1 158.4(1), Ga1−Ga2−C2 159.0(1).

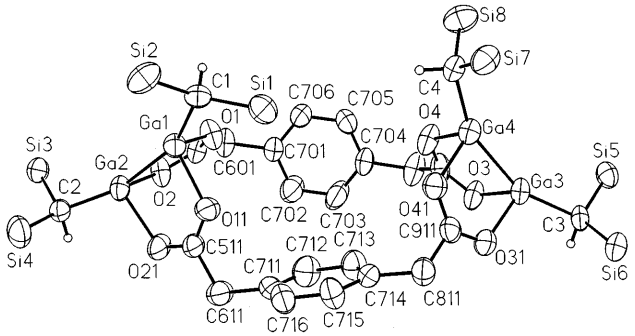
the angles between the chelating ligands show values of 88.5° and 87.3° in **3** and 88.2° in **4**.

These digallium dicarboxylato groups are bridged by a dimethylbenzene group in compound **3** to form a macrocycle containing 22 atoms. The aromatic rings do not, however, adopt the parallel arrangement, which is often observed in phenyl compounds and is caused by weak interactions between the delocalized π electrons, but the rings are perpendicular to one another with an angle between the normals of the planes of 93.1°. The reason is the very long distance between the aromatic rings (C701−C711 583 pm) forced by the geometry of the coordination of the Ga atoms. This distance is much longer than detected or calculated for compounds with a bonding interaction between phenyl groups, in which the separation between the carbon atoms of the phenyl rings is below 400 pm[8]. As can be seen from Figure 2 a quite unsymmetric molecular structure results in the solid state with the Ga−Ga bonds not arranged parallel, but their vectors subtend an angle of 94.4°.

In contrast, **4**, which has bridging cyclohexane groups, is a highly symmetric compound (Figure 3). **4** is located on a crystallographic center of symmetry, and the Ga−Ga bonds adopt a parallel arrangement. The cyclohexane rings have a chair conformation, and one bond to a carbonyl group occupies an axial position (C5−C51), while the other one (C54−C6′) is in an equatorial position. From this conformation, an almost rectangular cage results in the center of the molecule.

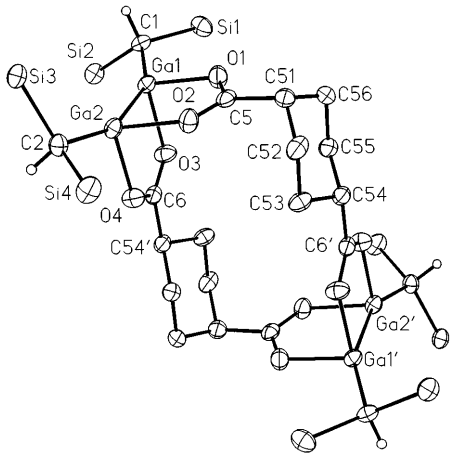
The results described here clearly confirm that the reaction of digallane(4) **1** with dicarboxylic acids is a powerful method for the synthesis of large macrocycles. It is of particular interest now to synthesize corresponding macrocyclic compounds that contain heteroatoms like N or S and could possibly act as ligands for the complexation of cations.

Figure 2. Molecular structure and numbering scheme of compound **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga1−Ga2 238.29(8), Ga3−Ga4 237.41(9), Ga1−O1 199.6(3), Ga1−O11 200.2(3), Ga1−C1 194.9(5), Ga2−O2 201.1(3), Ga2−O21 201.5(3), Ga2−C2 194.6(4), Ga3−O3 200.7(3), Ga3−O31 200.3(3), Ga3−C3 195.4(4), Ga4−O4 201.0(3), Ga4−O41 201.0(4), Ga4−C4 195.0(5), mean values: Ga−Ga−O 88.0, O−Ga−O 91.8, Ga−Ga−C 156.6.

Figure 3. Molecular structure and numbering scheme of compound **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga1−Ga2 237.46(4), Ga1−O1 202.9(2), Ga1−O3 199.7(2), Ga1−C1 195.2(2), Ga2−O2 199.8(2), Ga2−O4 201.1(2), Ga2−C2 195.8(2), O1−Ga1−O3 91.30(8), O2−Ga2−O4 92.19(7), Ga2−Ga1−O1 87.83(5), Ga2−Ga1−O3 87.40(5), Ga1−Ga2−O2 88.16(5), Ga1−Ga2−O4 88.48(5), Ga2−Ga1−C1 155.22(7), Ga1−Ga2−C2 156.37(7).

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Experimental Section

General: All procedures were carried out under purified argon in dried solvents (diisopropyl ether and toluene with Na/benzophenone, *n*-pentane with $LiAlH_4$). Compound **1** was synthesized as described in ref.[1], commercially available 1-adamantanecarboxylic acid, 1,4-benzenedi(methylcarboxylic) acid, and 1,4-butanedicarboxylic acid were sublimed in vacuo before use, and 1,6-hexanedicarboxylic acid and 1,4-cyclohexanedicarboxylic acid were used without further purification.

Reaction of **1** *with 1-Adamantanecarboxylic Acid, Synthesis of* **2**: Solid 1-adamantanecarboxylic acid (0.207 g, 1.15 mmol) was added

Table 1. Crystal data and data-collection parameters for **2**, **3**, and **4**

	2	**3**	**4**
Formula	$C_{36}H_{68}O_4Ga_2Si_4$	$C_{48}H_{92}Ga_4O_8Si_8$	$C_{44}H_{96}Ga_4O_8Si_8$
Crystal system	triclinic	triclinic	triclinic
Space group	P−1; No. 2 [9]	P−1; No. 2 [9]	P−1; No. 2 [9]
Z	2	2	1
T [K]	293(2)	293(2)	213(2)
$d_{calcd.}$ [g/cm^3]	1.231	1.241	1.283
a [pm]	1270.3(3)	1361.0(1)	1099.7(1)
b [pm]	1306.2(3)	1403.2(1)	1203.6(1)
c [pm]	1499.9(3)	1926.8(2)	1368.1(1)
α [°]	102.06(3)	72.940(9)	64.19(1)
β [°]	112.35(3)	84.33(1)	86.78(1)
γ [°]	96.08(3)	82.49(1)	89.69(1)
V [10^{-30} m^3]	2203.2(8)	3480.5(5)	1627.2(2)
μ [mm^{-1}]	1.364	1.709[a]	1.826[a]
Crystal size [mm]	0.30 × 0.30 × 0.76	0.23 × 0.30 × 0.38	0.45 × 0.50 × 0.80
Diffractometer	AED 2	AED 2	IPDS
Radiation	Mo-K_α; graphite monochromator		
Range	$3 \le 2\Theta \le 48°$	$3° \le 2\Theta \le 46°$	$4.8° \le 2\Theta \le 52°$
Reciprocal space	$-14 \le h \le 13$	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-14 \le k \le 14$	$-14 \le k \le 15$	$-14 \le k \le 14$
	$0 \le l \le 17$	$0 \le l \le 21$	$-16 \le l \le 16$
Scan mode	ω−2Θ	ω−2Θ	157 exposures; Δφ 1.4°
Independent reflections	6892	9624	5892
Number of reflections with $F > 4\,\sigma(F)$	5603	6907	4949
Parameters	546	637	301
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ $[F > 4\,\sigma\,(F)]$	0.0438	0.0534	0.0301
$wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w\,(F_o^2)^2\}^{1/2}$ (all data)	0.0782	0.0792	0.0588
Max./min. residual [10^{30} e/m^3]	0.724/−0.283	0.472/−0.279	0.590/−0.482

[a] Empirical absorption correction. − [b] Program: SHELXTL, SHELXL-93[10]; solutions by direct methods; full matrix refinement with all independent structure factors.

to a cooled (−50°C) solution of yellow digallane(4) **1** (0.445 g, 0.574 mmol) in 25 ml of *n*-pentane. The mixture was stirred and slowly warmed to room temperature. The color changed from yellow to colorless at a temperature of −15°C. The solvent was distilled off in vacuo, the residue was thoroughly dried in vacuo and recrystallized from *n*-pentane (20/−30°C). Yield: 0.370 g (79%), colorless crystals. − M. p. (argon, sealed capillary): 174°C. − ^{1}H NMR (C_6D_6, 300 MHz): δ = 2.02 (12 H, CH_2 of adamantyl), 1.85 (6 H, CH of adamantyl), 1.54 (12 H, CH_2 of adamantyl), 0.35 (36 H, $SiMe_3$), −0.30 (2 H, $GaCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 190.1 (CO_2), 41.9 (*ipso*-C of adamantyl, 39.7, 36.7, and 28.4 (adamantyl), 4.0 ($GaCSi_2$), 3.5 ($SiMe_3$). − IR (CsBr, paraffin): $\tilde{\nu}$ = 1580 vw, 1530 s cm^{-1} νCO_2; 1462 vs, 1377 vs paraffin; 1310 s, 1256 s, 1242 s δCH_3; 1186 vw, 1181 vw, 1169 vw, 1113 w, 1105 w, 1090 w νCC; 1015 vs δCH; 976 m, 949 s, 907 w, 843 vs, 797 s, 775 s, 758 s, 723 m ρCH_3(Si); 679 s, 671 s ν_{as}SiC; 627 w, 613 w ν_sSiC; 515 s, 500 s, 465 w, 422 m νGaC, νGaO; 370 vw, 355 vw, 339 vw δSiC. − MS (CI, three most intensive peaks): 815.1, 817.1, 818.1 (all M^+ + H) corresponding with a calculated isotope pattern. − $C_{36}H_{68}O_4Si_4Ga_2$ (816.7): calcd. Ga 17.1, found Ga 16.9. − Mol. mass: 769 (cryoscopically in benzene).

Reaction of **1** *with Ddicarboxylic Acids, General Procedure for the Syntheses of the Compounds* **3** *to* **6**: The solid dicarboxylic acids were added to a cooled (−50°C) solution of an equimolar quantity of yellow digallane(4) **1** (about 0.5 g) in 25 ml of *n*-pentane. The mixtures were warmed to room temperature and stirred for 2 d (**4**) or heated under reflux for 1.5 h (**5** and **6**) or 14 h (**3**). The color changed in each reaction from yellow to colorless. A small quantity of an unknown solid precipitated during the synthesis of **3**, which was filtered off. The filtrate was concentrated and cooled to −50°C to obtain colorless crystals of **3**. The other reaction mixtures were evaporated to dryness and thoroughly dried in vacuo to completely remove $CH_2(SiMe_3)_2$. The residues were recrystallized from different solvents (20/−30°C): **4** from toluene, **5** from diisopropyl ether and **6** from *n*-pentane.

Characterization of **3**: Yield: 83%, colorless crystals. − M. p. (argon, sealed capillary): 140°C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 6.88 (8 H, phenyl), 3.37 (8 H, CH_2), 0.27 (72 H, $SiMe_3$), −0.31 (4 H, $GaCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 184.3 (CO_2), 133.2 (*ipso*-C of phenyl), 129.2 (2,3,5,6-C of phenyl), 42.9 (CH_2), 4.5 ($GaCSi_2$), 3.3 ($SiMe_3$). − IR (CsBr, paraffin): $\tilde{\nu}$ = 1549 s cm^{-1} νCO_2; 1462 vs, 1377 vs paraffin; 1292 m, 1262 sh, 1246 s δCH_3; 1204 w, 1181 vw, 1165 vw, 1117 vw, 1078 vw νCC; 1013 s δCH; 930 m, 868 s, 843 vs, 787 m, 775 m, 758 s, 727 s ρCH_3(Si); 687 m, 669 s ν_{as}SiC; 638 w, 625 m, 611 w ν_sSiC; 563 vw, 523 m, 463 w, 422 w νGaC, νGaO; 378 vw, 353 vw, 334 vw δSiC. − MS (CI, three most intensive peaks): 1299.0, 1301.0, 1302.6 (all M^+ + H) corresponding with a calculated isotope pattern. − $C_{48}H_{92}O_8Si_8Ga_4$ (1300.8): calcd. Ga 21.4, found Ga 21.0. − Mol. mass: 1262 (cryoscopically in benzene).

Characterization of **4**: Yield: 85%, colorless crystals. − M. p. (argon, sealed capillary): 192°C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 2.2 to 1.2 (very broad, 20 H, cyclohexyl), 0.30 (72 H, $SiMe_3$), −0.47 (4 H, $GaCHSi_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 186.7 (CO_2), 41.7 (*ipso*-C of cyclohexyl), 26.8 (2,3,5,6-C of cyclohexyl), 4.2 ($GaCSi_2$), 3.4 ($SiMe_3$). − IR (CsBr, paraffin): $\tilde{\nu}$ = 1603 vw, 1539 w cm^{-1} νCO_2; 1462 vs, 1377 vs paraffin; 1304 w, 1258 sh, 1248 w δCH_3; 1204 vw, 1145 w, 1113 m, 1082 s, 1040 s νCC; 1013 s δCH; 918 w, 845 m, 791 w, 777 w, 758 w, 721 m ρCH_3(Si); 687 vw, 673 w, 669 w ν_{as}SiC; 627 w ν_sSiC; 517 s, 461 s νGaC, νGaO; 382 vw, 345 vw δSiC. − $C_{44}H_{96}O_8Si_8Ga_4$ (1256.8): calcd. Ga 22.2, found Ga 22.1. − Mol. mass: 1205 (cryoscopically in benzene).

Characterization of **5**: Yield: 86%, colorless crystals. − M. p. (argon, sealed capillary): 130°C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 2.18 (t, 8 H, CH_2CO$_2$), 1.48 and 1.06 (each m, 8 H, CH_2CH_2), 0.32 (72 H, SiMe$_3$), −0.32 (4 H, GaCHSi$_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 186.2 (CO_2), 36.5, 28.9 and 25.7 (CH_2), 4.3 (GaCSi$_2$), 3.4 (SiMe$_3$). − IR (CsBr, paraffin): $\tilde{\nu}$ = 1611 w, 1543 s cm^{-1} νCO_2; 1464 vs, 1377 vs paraffin; 1307 m, 1302 w, 1258 sh, 1248 s δCH$_3$; 1167 w, 1140 w, 1098 w, 1080 w νCC; 1015 s δCH; 939 m, 934 m, 843 vs, 785 m, 777 m, 758 m, 721 m ρCH$_3$(Si); 673 m ν_{as}SiC; 625 w, 613 w ν_sSiC; 525 vw, 515 w, 463 vw, 422 vw νGaC, νGaO; 388 vw, 338 vw δSiC. − $C_{44}H_{100}O_8Si_8Ga_4$ (1260.1): calcd. Ga 22.1, found Ga 22.3. − Mol. mass: 1135 (cryoscopically in benzene).

Characterization of **6**: Yield: 85%, colorless crystals. − M. p. (argon, sealed capillary): 125°C (dec.). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 2.10 (m, 8 H, CH_2CO$_2$), 1.41 (m, 8 H, CH_2CH_2), 0.30 (72 H, SiMe$_3$), −0.33 (4 H, GaCHSi$_2$). − ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 185.7 (CO_2), 36.2 and 25.1 (CH_2), 4.3 (GaCSi$_2$), 3.3 (SiMe$_3$). − IR (CsBr, paraffin): $\tilde{\nu}$ = 1545 m cm^{-1} νCO_2; 1458 vs, 1377 vs paraffin; 1331 w, 1312 m, 1248 s δCH$_3$; 1196 vw, 1150 w, 1113 w, 1082 w νCC; 1013 s δCH; 947 m, 932 m, 843 vs, 775 w, 758 m, 721 m ρCH$_3$(Si); 673 m ν_{as}SiC; 625 m, 613 w ν_sSiC; 523 w, 515 w, 463 w, 428 w, 401 vw νGaC, νGaO; 353 vw, 345 vw δSiC. − $C_{40}H_{92}O_8Si_8Ga_4$ (1204.7): calcd. Ga 23.1, found Ga 22.9. − Mol. mass: 1143 (cryoscopically in benzene).

Crystal Structure Determinations: Single crystals of the compounds **2**, **3**, and **4** were obtained by recrystallization from cyclopentane, diisopropyl ether, and toluene, respectively. Crystal data and structure refinement parameters are given in Table 1[11]. The adamantyl groups in **2** are rotationally disordered, and the carbon atoms with the exception of those attached to the carbonyl groups (C51 and C61) were refined in two positions with occupancy factors of 0.5. **4** is located on a crystallographic inversion center.

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[11] The crystallographic data of **2**, **3** and **4** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102026 (**2**), -102027 (**3**), and -102028 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, UK [Fax: Int. Code+(1223) 336−033; E-mail: deposit@chemcrys.cam.ac.uk].

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