A Carbon-Bridged Digallium Compound as a Chelating Lewis Acid: Complexation of Thiophenolate and Benzoate Anions by $H_5C_6{-}CH_2{-}C(SiMe_3)[Ga(CH_2tBu)_2]_2$

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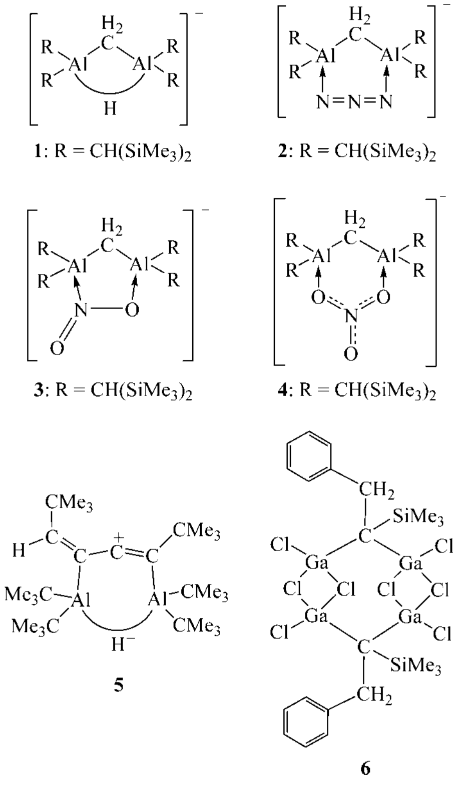
The digallium compound $H_5C_6{-}CH_2C(SiMe_3)(GaCl_2)_2$ (**6**) is easily available by the 2-fold hydrogallation of phenyl(trimethylsilyl)ethyne with $H{-}GaCl_2$. Its treatment with neopentyllithium gave the corresponding tetraneopentyl compound **7** by the replacement of all four chlorine atoms. Compound **7** has two coordinatively unsaturated gallium atoms attached to one carbon atom and, hence, is suitable to act as a chelating Lewis acid. Accordingly, tetrabutylammonium thiophenolate dissolved in 1,2-difluorobenzene reacted readily with **7** to afford the adduct **8**, in which the sulfur atom of the thiophenolato group is coordinated by both gallium atoms to form a four-membered CGa_2S heterocycle. A similar compound (**9**) was formed upon treatment of **7** with the benzoate anion. A slightly different structural motif compared to **8** resulted because each oxygen atom of the benzoate ligand is coordinated to one gallium atom to give a six-membered $Ga_2C_2O_2$ heterocycle.

Introduction

Compounds containing more than one coordinatively unsaturated atom of a group 13 element in a single molecule are potentially useful as effective chelating Lewis acids. They found increasing interest in recent literature because they may be applicable in phase transfer processes, in anion recognition, or in catalysis.[1,2] However, the true capability of these compounds to act as polyacceptors was tested in only a few cases.[1–3] One impressive example is a methylene-bridged dialuminium compound, $R_2Al{-}CH_2{-}AlR_2$ [$R = CH(SiMe_3)_2$], which was obtained in our group several years ago.[2] Its synthesis required very bulky bis(trimethylsilyl)methyl substituents in order to prevent decomposition by dismutation. It formed persistent adducts by the chelating coordination of anions such as hydride, azide, nitrite, or nitrate (**1** to **4**; Scheme 1).[3] Sodium nitrate, for instance, dissolved readily in ethereal solutions by the addition of that particular dialuminum compound.[3] Further, the importance and efficiency of chelating anion coordination by dialuminum compounds was shown with the syntheses of stable carbocationic species in which the formation of the Al−H−Al

Scheme 1



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bridge is favored over the formation of a C−H bond (**5**).[4] In order to synthesize a broader variety of chelating Lewis acids possessing more than two aluminum or gallium atoms, we tried to apply the hydroalumination or hydrogallation of oligoalkynes with dialkylelement hydrides. But these reactions proved to be much more complicated and interesting than may be derived from textbook knowledge. Instead of the expected simple addition products, we isolated fascinating novel compounds such as carbaalane clusters[5,6] or cyclophane-type molecules[7,8] by condensation processes. With few exceptions[8] only trimethylsilyl alkynes yielded the expected alkenylaluminum or -gallium compounds, $H_{6-x}C_6[-C(H){=}C(SiMe_3)(ER_2)]_x$, upon treatment with aluminum or gallium hydrides.[9] While the corresponding trialkylelement compounds were not released in these cases, *cis*/*trans* isomerization at the C=C double bonds occurred. The course of the rearrangement depended on the bulkiness of the element hydrides, and a persistent *cis* arrangement of the ER_2 groups (E = Al, Ga) and the hydrogen atoms resulted only for the sterically most shielded di(*tert*-butyl) compounds. This observation may indicate that the isomerization is initiated by some intermolecular activation. For steric reasons only the *trans* forms are potentially applicable as chelating Lewis acids, but we did not succeed in isolating any pure adduct derived from dialkylaluminum or -gallium derivatives.

In recent investigations we showed that $H{-}GaCl_2$[10] is a very interesting alternative reagent for the hydrogallation of silylalkynes.[11] It afforded selectively the expected monoaddition products that had the gallium atoms in geminal positions to the trimethylsilyl groups. Gallium and hydrogen atoms adopted a *trans* arrangement across the C=C double bonds.[11] The 2-fold hydrogallation of an alkyne did not succeed even on employing large excesses of dialkylaluminum or dialkylgallium hydrides. However, the complete reduction of the triple bonds with the formation of alkane derivatives was easily achieved with the dichloro compound.[12] The products obtained by these reactions formed interesting dimeric structures (**6**, Scheme 1) and were able to coordinate chloride anions in a chelating manner.[12] Furthermore, they may be suitable starting compounds for the generation of alkyl derivatives by reactions with alkyllithium derivatives and salt elimination. First results are reported here.

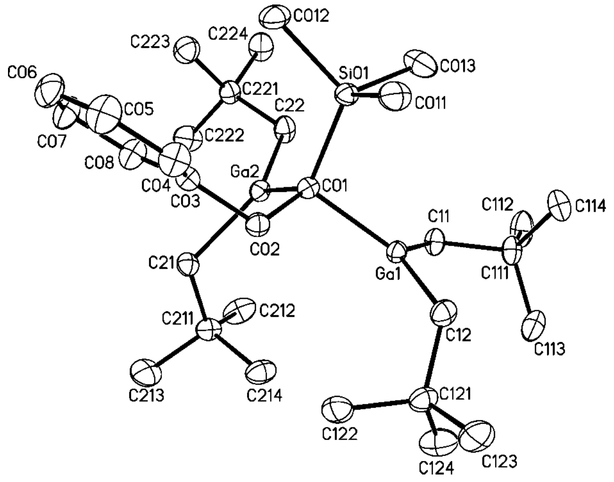
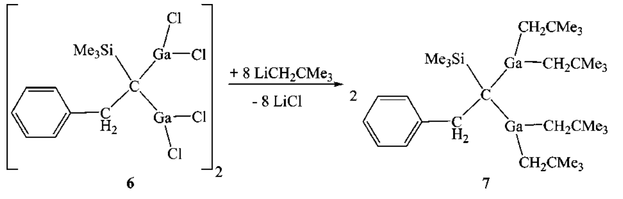


Figure 1. Molecular structure of **7**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(11) 1.991(2), Ga(1)−C(12) 1.999(2), Ga(1)−C(01) 2.017(2), Ga(2)−C(21) 2.005(2), Ga(2)−C(22) 1.992(2), Ga(2)−C(01) 1.986(2), C(01)−Si(01) 1.880(2), Ga(1)−C(01)−Ga(2) 103.58(9), C(11)−Ga(1)−C(12) 125.8(1), C(21)−Ga(2)−C(22) 121.8(1), C(01)−C(02)−C(03) 117.4(2).

Results and Discussion

Generation of the Tetraneopentyldigallium Compound 7. The tetrachlorodigallium starting compound **6** is available on a facile route by the treatment of phenyl(trimethylsilyl)ethyne with 2 equiv of $H{-}GaCl_2$ in boiling *n*-hexane.[12] Reaction of **6** with 4 equiv of neopentyllithium afforded colorless crystals of the tetraneopentyl compound **7** in an excellent yield of 86% (eq 1). The ^1H NMR spectroscopic characterization verified the formation of **7** by the correct integration ratio of its signal intensities. Singlets resulted for the trimethylsilyl and *tert*-butyl groups and for that methylene group that bridges the gallium atoms and the phenyl ring. The methylene protons of the neopentyl groups become diastereotopic and gave two doublets at $\delta = 1.25$ and 1.40 with a coupling constant of 13.2 Hz. In the ^{13}C NMR spectrum the resonance of the inner carbon atom attached to one silicon and two gallium atoms occurs at a relatively low field ($\delta = 49.4$). These values correlate to the number of gallium atoms attached to a single carbon atom, and even stronger shifts to $\delta = 95$ were detected for trigallium compounds.[6]



(1)

The molecular structure of compound **7** is depicted in Figure 1. It has two dialkylgallium groups attached to that carbon atom that also bears the trimethylsilyl group. Formally it may be described as the product of a 2-fold hydrogallation of phenyl(trimethylsilyl)ethyne with dineopentylgallium hydride. However, as mentioned before, such a reaction does not succeed on a direct route. To the best of our knowledge, compounds similar to **7** having two coordinatively unsaturated dialkylgallium groups bonded to one central carbon atom are not known in the

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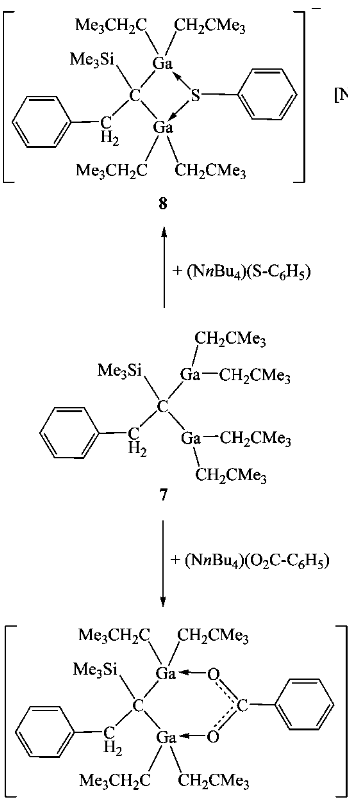
literature. Heteroadamantane cages of the type $(GaR)_6(CR')_4$ were described that had carbon atoms coordinated to three unsaturated gallium atoms.[6] The distance (bite) between both gallium atoms in **7** is 3.14 Å. The Ga−C−Ga angle (103.6°) deviates slightly from the ideal tetrahedral angle. The Ga−C bond lengths are quite similar (1.998 Å on average) and correspond well to standard values.

Application of the Digallium Compound 7 as a Chelating Lewis Acid. The digallium compound **7** has two coordinatively unsaturated gallium atoms in a distance of 3.14 Å. This particular arrangement should allow for an efficient chelating coordination of single atoms or small molecules and anions. In preliminary experiments we treated **7** with thiophenolate and benzoate anions (eq 2), which had tetrabutylammonium counterions in order to enhance their solubility in common organic solvents. The corresponding adducts **8** and **9** were isolated in 72% and 50% yields after recrystallization. The synthesis of compound **9** succeeded in toluene, from which the product separated upon cooling as a highly viscous liquid. Interestingly, 1,2-difluorobenzene, which is relatively polar, but does not have donor properties, proved to be the best solvent for the generation of **8**. In both cases purification was achieved by recrystallization from 1,2-difluorobenzene. The molecular symmetry and the shape of the NMR spectra changed dramatically by the chelating coordination of the anions. However, complete NMR spectroscopic characterization succeeded only with compound **9**, while independently of the solvent too many and in part relatively broad resonances resulted in the spectra of the thiophenolato derivative **8**. Only the signals of the butyl groups of the cation were clearly resolved in that case. Temperature-dependent NMR spectra did not help for a better understanding. The best ^{1}H NMR spectrum was recorded in CD_2Cl_2, the results of which are given in the Experimental Section. These difficulties may be caused by the slow decomposition observed in solution at room temperature and by some dynamic effects, which both may be influenced by the insufficient correspondence of the bite between both gallium atoms and the covalence radius of the sulfur atom (see below). Hence, characterization of **8** is restricted to elemental analysis and crystal structure determination. **8** is stable in the solid state over months.

In contrast, clearly resolved spectra were determined for compound **9**. Caused by the fixed conformation in the resulting heterocycle, the neopentyl groups attached to one gallium atom became chemically different and show two independent sets of resonances. Two neopentyl groups are neighboring the trimethylsilyl residue, while the two remaining ones are on the same side of the heterocycle as the benzyl group. The lack of mirror planes in the molecules and the prochiral character of the carbon atoms in the heterocycles cause the splitting of the methylene hydrogen atoms of the neopentyl groups, which show two pairs of doublets in the ^{1}H NMR spectra. Compared to the neutral starting compound **7**, the most dramatic alteration of a chemical shift was observed for the carbon atom attached to both gallium atoms ($\delta = 49.4$ for **7** to 19.0 for **9**). This shift to a higher field is in accordance with former observations and indicates an enhancement of the coordination numbers of the gallium atoms from three to four.[13]



(2)

Both adducts were characterized by crystal structure determinations (Figures 2 and 3). The sulfur atom of the thiophenolato ligand in **8** is coordinated in a chelating manner by both gallium atoms to afford a folded four-membered Ga_2CS heterocycle. The Ga−S distances (2.534 Å on average) are considerably longer than generally observed for thiolato-bridged digallium compounds.[14] This may be caused by the chelating coordination of the sulfur atom and the insufficient coincidence of the relatively rigid bite of the ligand and the covalence radius of the sulfur atom. Further, the sulfur atom has a pyramidal coordination sphere, and there may be a repulsive interaction between the hydrogen atoms of the phenyl and neopentyl groups. The increase of the coordination numbers of the gallium atoms from three in **7** to four in **8** results in the expected lengthening of the Ga−C bonds by up to 0.04 Å. The strongest effect occurs for the bridging carbon atom in the ring. Caused by the chelating coordination of the anion, the angle Ga−C−Ga decreased from 103.6° in **7** to 97.0° in the adduct **8**. The most acute angle of the heterocycle appeared at the sulfur atom (74.5°). Each oxygen atom of the carboxylato group in compound **9** (Figure 3) is coordinated to one gallium atom of the dipodal chelating Lewis acid **7**. Thus, in this case a six-membered $Ga_2C_2O_2$ heterocycle resulted by adduct formation. The ring is not planar with the carbon atom C1 0.69 Å above the average plane spanned by the remaining five atoms. Due to the higher coordination numbers at the gallium atoms, the Ga−C bonds are lengthened by up to 0.04 Å compared to the starting compound **7**. The Ga−O bond lengths (2.037 Å) are a little longer than in carboxylato-bridged digallium compounds possessing Ga−Ga bonds and correspond to distances observed for the terminal coordination of a single gallium atom by a chelating carboxylato

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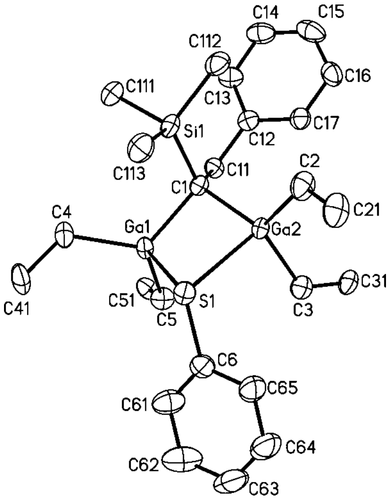

Figure 2. Molecular structure of **8**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 2.057(3), Ga(1)−C(4) 2.023(4), Ga(1)−C(5) 2.027(4), Ga(2)−C(1) 2.036(3), Ga(2)−C(2) 2.028(4), Ga(2)−C(3) 2.014(4), C(1)−Si(1) 1.856(3), Ga(1)−C(1)−Ga(2) 97.0(1), C(1)−Ga(1)−S(1) 88.20(9), C(1)−Ga(2)−S(1) 88.1(1), Ga(1)−S(1)−Ga(2) 74.46(3).

ligand.[15,16] The angle O−C−O (126.6°) is relatively inflexible and similar to those observed for other gallium compounds.[16] The Ga−C−Ga angle increased by about 2° compared to **7** (105.4°).

Experimental Section

All procedures were carried out under purified argon. Toluene was dried over Na/benzophenone; 1,2-difluorobenzene, over molecular sieves. $H_5C_6{-}CH_2{-}C(SiMe_3)(GaCl_2)_2$[12] and neopentyllithium[17]were obtained according to literature procedures. The commercially available compounds tetrabutylammonium thiophenolate and benzoate were thoroughly evacuated prior to use. Only the most intensive peaks of the mass spectrum of **7** are given; the complete isotopic patterns are in accordance with the calculated ones. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Synthesis of 7. Compound **6** (1.58 g, 3.46 mmol) was dissolved in 200 mL of warm toluene (50 to 60 °C). After cooling to –80 °C neopentyllithium (1.08 g, 13.8 mmol) dissolved in 25 mL of toluene was added dropwise. The reaction mixture was warmed to room temperature and stirred for 24 h. About 150 mL of the solvent were removed under vacuum, and the remaining suspension was filtered. Further concentration of the filtrate to a few milliliters and cooling to −45 °C yielded colorless crystals of compound **6**. Yield: 1.78 g (86%). Mp (argon, sealed capillary): 82 °C. Anal. Calcd [$C_{31}H_{60}SiGa_2$] (599.4): C, 62.02; H, 10.07; Ga, 23.23. Found: C, 61.7; H, 10.1; Ga, 23.1. ^1H NMR (C_6D_6, 400 MHz): δ 7.19 (2 H, m, *meta*-H of phenyl), 7.15 (2 H, m, *ortho*-H of phenyl), 7.05 (1 H, m, *para*-H of phenyl), 4.12 (2 H, s, CH_2-Ph), 1.40 and 1.25 (each 4 H, d, $^2J_{HH}$ = 13.2 Hz, $GaCH_2t$Bu), 1.22 (36 H, s, *t*Bu), 0.23 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 146.2 (*ipso*-C of phenyl), 128.9 (*meta*-C of phenyl), 128.2 (*ortho*-C of phenyl), 126.5 (*para*-C of phenyl), 49.4 (GaCGa), 42.4 ($GaCH_2t$Bu), 39.7 ($GaCH_2$Ph), 35.1 (CMe_3), 32.9 (CMe_3), 4.5 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79 MHz): δ –4.9. IR (CsBr plates, paraffin, cm^{-1}): 1954 w, 1937 w, 1856 w, 1790 w, 1728 vs, 1601 s, 1582 m, 1493 s (phenyl); 1465 vs (paraffin); 1385 s $\delta(CH_3)$; 1360 vs (paraffin); 1332 w, 1287 s, 1258 vs, 1244 vs, 1226 vs $\delta(CH_3)$; 1132 vs, 1103 s, 1076 m, 1051 w, 1015 s, 1001 s, 974 s, 949 s, 932 m ν(CC), ν(CN); 908 w, 899 m, 841 vs, 746 vs, 730 vs $\rho(CH_3(Si))$; 720 vs (paraffin); 698 vs, 667 s ν_{as}(SiC); 646 s, 608 s ν_s(SiC); 581 w, 544 s, 513 m, 460 s, 436 s ν(GaC), δ(CC). MS (EI, 70 eV) (%): 583 (1), 585 (2), 587 (1) $M^+ - Me$; 527 (70), 529 (100), 531 (39) $M^+ - SiMe_3$.

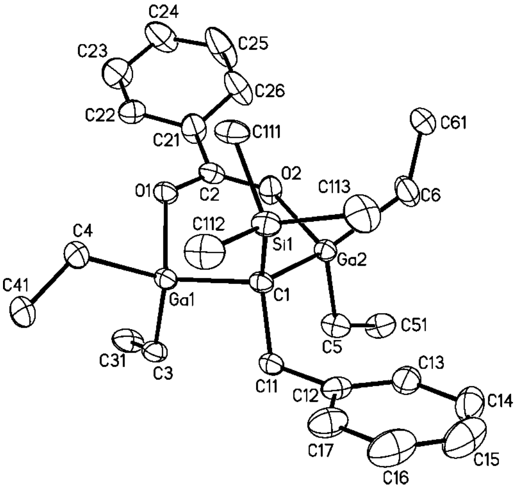

Figure 3. Molecular structure of **9**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 2.041(3), Ga(1)−C(3) 2.018(3), Ga(1)−C(4) 2.020(3), Ga(1)−O(1) 2.035(2), Ga(2)−C(1) 2.0483(3), Ga(2)−C(5) 2.026(3), Ga(2)−C(6) 2.019(3), Ga(2)−O(2) 2.039(2), C(1)−Si(1) 1.853(3), Ga(1)−C(1)−Ga(2) 105.4(2), C(1)−Ga(1)−O(1) 105.60(9), C(1)−Ga(2)−O(2) 105.7(1), Ga(1)−O(1)−C(2) 126.0(2), Ga(2)−O(2)−C(2) 133.3(2).

Synthesis of the Thiophenolato Adduct 8. Tetrabutylammonium thiophenolate (0.281 g, 0.80 mmol) was dissolved in 10 mL of 1,2-difluorbenzene. The mixture was added dropwise to a solution of the digallium compound **7** (0.480 g, 0.80 mmol) in 20 mL of the same solvent at room temperature. After stirring for 3 h the solution was concentrated to a few milliliters and cooled to 4 °C to yield colorless crystals of **8**. Yield: 0.55 g (72%). **8** decomposes slowly in solution, but is stable in the solid state. Mp (argon, sealed capillary): 126 °C. Anal. Calcd [$C_{53}H_{101}NSiSGa_2$] (950.4): C, 66.87; H, 10.69; Ga, 14.65; S, 3.37. Found: C, 66.5; H, 10.5; Ga, 13.7; S, 3.2. ^1H NMR (CD_2Cl_2, 400 MHz): δ 3.53 (2 H, s, CH_2-Ph), 2.99 (8 H, *pseudo*-t, NCH_2), 1.32 (8 H, m, NCH_2CH_2), 1.20 (8 H, m, $NCH_2CH_2CH_2$), 1.11 (36 H, s, CMe_3), 0.83 (12 H, t, $NCH_2CH_2CH_2CH_3$), –0.25 (9 H, s, $SiMe_3$); resonances of phenyl protons and of methylene protons of the neopentyl groups are not resolved; impurities by decomposition. IR (CsBr plates, paraffin, cm^{-1}): 1940 w, 1871 w, 1800 w, 1607 s, 1597 s, 1574 vs, 1492 s (phenyl); 1470 s, 1460 s, 1454 s (paraffin); 1447 s, 1418 w $\delta(CH_3)$; 1377 m (paraffin); 1354 m, 1331 vw, 1310 vw, 1226 vs $\delta(CH_3)$; 1179 w, 1152 m, 1132 m, 1107 m, 1082 s, 1028 m, 1021 m, 1007 m, 991 m, 943 m ν(CC), ν(CN); 903 m, 895 m, 880 m, 853 s, 826 s $\rho(CH_3(Si))$; 727 s (paraffin); 694 s, 668 s ν_{as}(SiC); 655 m, 633 w ν_s(SiC); 590 s, 530 m, 509 m, 480 m, 459 s, 422 m ν(GaC), δ(CC).

Synthesis of the Benzoato Adduct 9. Tetrabutylammonium benzoate (0.364 g, 1.00 mmol) was dissolved in 60 mL of toluene. The mixture was added dropwise to a solution of the digallium compound **7** (0.599 g, 1.00 mmol) in 60 mL of the same solvent. After stirring for 4 h at room temperature the reaction mixture was filtered. The filtrate was concentrated and cooled to –45 °C. An oily phase separated, which was isolated. A second fraction was

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Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 7, 8, and 9

	7	8	9
formula	$C_{31}H_{60}Ga_2Si$	$C_{56.5}H_{101}Ga_2NSSi$	$C_{54}H_{101}Ga_2NO_2Si$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
temp, K	153(2)	153(2)	153(2)
D_{calcd}, g/cm^3	1.163	1.089	1.101
a, Å	12.112(2)	14.202(2)	11.476(2)
b, Å	18.898(3)	20.403(3)	21.410(3)
c, Å	15.118(2)	21.021(3)	23.672(3)
α, deg	90	90	90
β, deg	97.756(3)	95.521(3)	90.414(3)
γ, deg	90	90	90
V, 10^{-30} m^3	3428.7(9)	6063(2)	5816(1)
μ, mm^{-1}	1.622	0.975	0.982
cryst dimens, mm	0.90 × 0.40 × 0.20	0.18 × 0.18 × 0.02	0.30 × 0.08 × 0.06
radiation	Mo Kα; graphite monochromator		
θ range, deg	1.73 – 30.13	1.66 – 30.05	1.28 – 30.06
index ranges	$-16 \le h \le 17$ $-26 \le k \le 26$ $-21 \le l \le 21$	$-19 \le h \le 19$ $-28 \le k \le 28$ $-29 \le l \le 29$	$-16 \le h \le 15$ $-29 \le k \le 28$ $-32 \le l \le 32$
no. of unique reflns	10 035 [R_{int} = 0.0559]	17 683 [R_{int} = 0.0843]	16 832 [R_{int} = 0.0968]
no. of params	322	562	617
R1 (reflns $I > 2\sigma(I)$)	0.0428 (7367)	0.0681 (10146)	0.0584 (9593)
wR2 (all data)	0.1018	0.1801	0.1376
max./min. residual electron density, 10^{30} e/m^3	1.101/−0.449	1.819/−0.548	0.736/−0.372

obtained after further concentration of the solution. The oily phases were dissolved in 1,2-difluorobenzene. Colorless crystals of **9** were isolated upon cooling to −4 °C. Yield: 0.470 g (50%). Mp (argon, sealed capillary): 139 °C. Anal. Calcd [$C_{54}H_{101}NO_2SiGa_2$] (962.4): C, 67.29; H, 10.56; Ga, 14.47. Found: C, 67.3; H, 10.8; Ga, 14.3. ^{1}H NMR (C_6D_6/1,2-$F_2C_6H_4$, 400 MHz): δ 8.52 (2 H, m, *ortho*-H of benzoate), 7.72 (2 H, *pseudo*-d, *ortho*-H of benzyl), 7.19 (2 H, m, *meta*-H of benzyl), 7.17 (1 H, m, *para*-H of benzoate), 7.16 (2 H, m, *meta*-H of benzoate), 7.00 (1 H, m, *para*-H of benzyl), 3.95 (2 H, s, C*H*$_2$-Ph), 2.27 (8 H, t, NC*H*$_2$), 1.55 and 1.50 (each 18 H, s, *t*Bu), 1.40 and 1.30 (each 2 H, d, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$-*t*Bu), 1.41 and 1.15 (each 2 H, d, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$*t*Bu), 1.06 (8 H m, $NCH_2CH_2CH_2$ (C*H*$_2$)), 0.98 (8 H, m, NCH_2CH_2 (C*H*$_2$)), 0.80 (12 H, t, $NCH_2CH_2CH_2CH_3$ (C*H*$_3$)), 0.32 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6/1,2-$F_2C_6H_4$, 100 MHz): δ 173.4 (CO_2), 150.8 (*ipso*-C of benzyl), 137.0 (*ipso*-C of benzoate), 131.0 (*ortho*-C of benzyl and benzoate), 130.9 (*para*-C of benzoate), 127.9 (*meta*-C of benzoate), 127.6 (*meta*-C of benzyl), 124.4 (*para*-C of benzyl), 58.5 (N*C*H$_2$), 41.7 (Ph*C*H$_2$), 37.2 and 35.7 (*t*Bu*C*H$_2$), 36.1 and 35.8 (C*Me*$_3$), 33.6 and 33.0 (*C*Me$_3$), 23.6 (NCH_2*C*H$_2$), 19.7 (NCH_2CH_2*C*H$_2$), 19.0 (Ga*C*Ga), 13.4 ($NCH_2CH_2CH_2$*C*H$_3$), 6.4 ($SiMe_3$). ^{29}Si NMR (C_6D_6/1,2-$F_2C_6H_4$, 79 MHz): δ –1.3. IR (CsBr plates, paraffin, cm^{-1}): 1597 s, 1562 s (phenyl); 1454 vs (paraffin); 1393 w δ(CH_3); 1377 s (paraffin); 1356 m, 1231 m δ(CH_3); 1173 w, 1152 w, 1128 w, 1117 w, 1105 w, 1067 w, 1026 w, 980 w, 932 w ν(CC), ν(CN); 907 w, 883 w, 851 m, 829 w, 756 m ρ(CH_3(Si)); 719 w (paraffin); 704 w, 677 w ν_{as}(SiC); 654 vw, 636 vw ν_s(SiC); 603 w, 590 w, 579 w, 540 w, 511 vw, 473 m, 447 w ν(GaC), δ(CC).

Crystal Structure Determinations of Compounds 7, 8, and 9. Single crystals of **7**, **8**, and **9** were obtained by recrystallization from toluene (20/−45 °C). The crystallographic data were collected with a Bruker APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97[18] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters, and structure refinement details are given in Table 1. The crystals of **8** enclosed a toluene molecule that was strongly disordered across a crystallographic center of symmetry. One *n*-butyl group of **9** showed a disorder; the atoms were refined on split positions. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-675459 (**7**), -675460 (**8**), and -675461 (**9**).

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Supporting Information Available: CIF files giving the crystal data for compounds **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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