4226 *Organometallics* **1998,** *17,* 4226−4231

Trimethylgallium-Induced Trimerization of Acetonitrile

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Received May 6, 1998

The reaction of $GaMe_3$ in acetonitrile in the presence of halide ions, F^-, Cl^-, and Br^-, at 60 °C gives the heterocycle $[Me_2Ga\{HNC(Me)\}_2C(CN)]$ (**1**). Further reaction with $GaMe_3$ and MeCN leads to a hexanuclear gallium complex $[(Me_2Ga)_4(MeGa)_2\{HNC(Me)C(CN)CH(NCMe)_2\}_2]$ (**2**). In addition to **2**, **2**·3MeCN and **2**·2$GaMe_3$ can be obtained under special conditions. **1** and **2** have been characterized by their NMR, IR, and MS spectra. X-ray analyses were performed with **1**, **2**, **2**·3MeCN, and **2**·2$GaMe_3$. Compound **1** consists of six-membered heterocycles, which are connected by hydrogen bridges to zigzag chains along the direction [010]. **2** contains 10 units of acetonitrile and six gallium centers forming a centrosymmetric eight-membered Ga−N ring. The structure of **2**·3MeCN exhibits two hydrogen-bridged MeCN molecules and one acetonitrile molecule which is not connected to another component of the unit cell. In **2**·2$GaMe_3$ two units of $GaMe_3$ are coordinated to the CN groups of **2** creating weakly pyramidalized $GaMe_3$ fragments.

Triorganohalometalates of group 13, first synthesized by Ziegler et al.,[1] can be used as a reservoir for the corresponding metallanes[2] and as a storage of low-temperature waste heat.[3] The basic structural motif in the Cs salts such as $Cs[Me_3MF]$ (M = Al, Ga, In),[4] $[Cs\{i\text{-}Pr_3MF\}]_4$,[5] $[Cs\{(PhCH_2)_3GaF\}]_2$·2MeCN,[6] and $[Cs\{(PhCH_2)_3InCl\}]_2$·0.5toluene[7] is a four-membered Cs_2X_2 ring (X = halide).

Interactions between Cs_2X_2 units can be avoided by the shielding of the rings through aryl ligands, forming Cs^+−π-electron contacts.[6,7] This principle also is the key for the synthesis of monomers such as $[Cs(toluene)_3(FIn\{N(SiMe_3)_2\}_3)]$.[8] Our standard reaction conditions for the preparation of the Cs salts involved reaction of MR_3 with CsX in acetonitrile at 20 °C. However, we found that reactions carried out at higher temperatures (50−60 °C) or at reflux conditions lead to dark brown solutions with a decreasing yield of the metalates. After more than 24 h reaction time almost no $GaMe_3$ (or $[Me_3GaX]^-$ and $[Me_3GaXGaMe_3]^-$, depending on the amount of halide ion) was detected. In this paper, the reaction products from the reaction system $GaMe_3$/acetonitrile/halide ion will be presented.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvents were performed using standard methods.[9] $GaMe_3$ was donated by the group of Prof. Dr. J. Lorberth.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer (^1H, 300.134 MHz; ^{13}C, 75.469 MHz). The standard is TMS (external) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). For the EI mass spectra, a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected). The cryoscopic measurements were performed using a Normag molecular weight determination apparatus combined with a Beckmann thermometer.

Synthesis of $[Me_2Ga\{HNC(Me)\}_2C(CN)]$, 1. A 6.38 g (55.6 mmol) amount of $GaMe_3$ and 0.17 g (1.1 mmol) of CsF were dissolved in 50 mL of MeCN, and the reaction mixture was stirred at 60 °C for 70 h. The solvent was removed under vacuum, and the brown residue was dissolved in 200 mL of toluene and filtered through silanized silica gel. After evaporation of the solvent, a colorless solid was isolated (7.6 g, 62% yield, mp 159 °C). ^1H NMR (toluene-d_8, ppm): −0.2 (s, 6 H, $GaCH_3$), 1.66 (s, 3 H, $NCCH_3$), 1.67 (s, 3 H, $NCCH_3$), 5.24 (s, 2 H, NH). ^{13}C (toluene-d_8, ppm): −5.1 ($GaCH_3$), 27.5 ($N{=}CCH_3$), 78.7 ($NCCC_2$), 121.5 (CN), 173.5 ($C{=}N$). Cryoscopic molecular weight (fw 221.94) [concentration (mol/L), wt, degree of association]: 0.0578, 222, 1.0. IR (Nujol, cm^{-1}): 3352 (s, ν_{NH}), 3258 (s, br, ν_{NH}), 2729 (w), 2403 (w), 2361 (w), 2255 (vw), 2199 (vs, $\nu_{C\equiv N}$), 2147 (m, $\nu_{C\equiv N}$), 1600 (vs, $\nu_{C=N}$), 1277 (vs), 1252 (vs), 1187 (vs), 1170 (s), 1151 (vs), 1094 (s), 1030 (vs), 1016 (vs), 933 (m), 851 (s), 800 (s), 746 (vs), 676 (s), 640 (vs), 604 (m), 565 (vs, $\nu_{as\ GaC_2}$), 543 (vs, $\nu_{s\ GaC_2}$), 525 (s), 459 (vs, $\nu_{ring\ GaN}$), 410 (s, $\nu_{ring\ GaN}$), 390 (s), 366 (m), 343 (m), 318 (m), 310 (m), 295 (m), 237 (vs), 218 (s), 188 (s), 163 (s), 143 (m), 114 (m). EI-MS (m/z (relative intensity), fragment): 221 (1), M^+; 206 (10), $(M - Me)^+$; 191 (2), $(M - 2Me)^+$; 165 (5), $(M - MeCN - Me)^+$; 150 (6), $(M - MeCN - 2Me)^+$; 99 (6), $(GaMe_2)^+$; 69 (17),

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† Dedicated to Prof. Dr. Johann Weidlein on the occasion of his 60th birthday.

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S0276-7333(98)00354-9 CCC: $15.00
Publication on Web 08/15/1998

Table 1. Crystallographic Data for the Compounds 1, 2, 2·3MeCN, and 2·2GaMe$_3$

	1	**2**	**2**·3MeCN	**2**·2GaMe$_3$
formula	$C_8H_{14}N_3Ga$	$C_{30}H_{52}N_{10}Ga_6$	$C_{36}H_{61}N_{13}Ga_6$	$C_{36}H_{70}N_{10}Ga_8$
fw	221.94	971.08	1094.29	1200.78
cryst size (mm)	0.3 × 0.4 × 0.2	0.3 × 0.15 × 0.3	0.55 × 0.3 × 0.15	0.12 × 0.1 × 0.1
a (pm)	1105.6(1)	1026.1(2)	1015.8(3)	995.5(1)
b (pm)	1362.6(1)	2169.7(4)	1539.0(3)	1051.2(1)
c (pm)	731.6(1)	1001.5(1)	1715.5(5)	1374.6(1)
α (deg)			75.97(1)	91.08(1)
β (deg)		111.70(1)	74.17(1)	106.60(1)
γ (deg)			79.62(1)	108.23(1)
V (pm^3 × 10^6)	1102.1(2)	2071.7(6)	2484(1)	1300.6(2)
space group	Pbcm	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
No.[23]	57	14	2	2
Z	4	2	2	1
ρ_{calcd} (g/cm^3)	1.338	1.557	1.463	1.533
temp (K)	190	193	223	190
abs corr	numerical	empirical	empirical	numerical
μ (cm^{-1})	24.5	46.0	32.4	41.1
radiation	Mo Kα	Cu Kα	Mo Kα	Mo Kα
$2\theta_{max}$ (deg)	51.62	110.0	50.0	51.86
h, k, l values	$-13 \le h \le 13$ $-16 \le k \le 16$ $-8 \le l \le 8$	$-10 \le h \le 10$ $-23 \le k \le 0$ $-10 \le l \le 0$	$-1 \le h \le 11$ $-17 \le k \le 17$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-12 \le k \le 12$ $-16 \le l \le 16$
no. of reflns	8627	2872	10 299	10 035
no. of unique reflns	1140	2601	8692	4743
no. of reflns with $F_o > 4\sigma(F_o)$ for R_1	967	2474	3539	3030
no. of params	102	212	491	249
R_1[a]	0.0273	0.0753	0.0724	0.0341
wR_2 (all data)[b,c]	0.0531	0.1738	0.2106	0.0746
weight factor a	0.0363	0.0439	0.1094	0.0346
weight factor b	0	39.76	0	0
max/min resid electron density (e/pm^3 × 10^6)	0.61/−0.43	0.78/−0.69	0.97/−2.1	0.55/−0.72

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_c|$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Ga^+; 41 (3), $(MeCN)^+$. Anal. Calcd: C, 43.29; H, 6.36; N, 18.93. Found: C, 42.99; H, 6.13; N, 18.90.

Synthesis of $[(Me_2Ga)_4(MeGa)_2\{HNC(Me)C(CN)CH(NCMe)_2\}_2]$, 2. A 2.0 g (17.4 mmol) amount of $GaMe_3$ and 0.074 g (0.35 mmol) of CsBr were dissolved in 50 mL of MeCN. The reaction mixture was stirred at 60 °C for 72 h, filtered, and cooled to −25 °C for 2 days. **2** crystallizes as amber-colored prisms (0.3 g, 10% yield based on $GaMe_3$). ^1H NMR (toluene-d_8, ppm): −0.41 (s, 12 H, $Ga(CH_3)_2$), −0.34 (s, 12 H, $Ga(CH_3)_2$), −0.32 (s, 6 H, $GaCH_3$), 1.48 (s, 6 H, $H_3CC{=}NH$), 1.85 (s, 12 H, $H_3CC{=}N$), 5.06 (s, br, 2 H, NH), 5.95 (s, 2 H, C_3CH). ^{13}C NMR (toluene-d_8, ppm): −4.7 ($Ga(CH_3)_2$), −4.5 ($Ga(CH_3)_2$), −4.2 ($GaCH_3$), 27.2 ($CH_3C{=}N$), 29.9 ($CH_3C{=}NH$), 68.2 (C_3CH), 77.3 ($CC{\equiv}N$), 123.0 ($C{\equiv}N$), 161.6 ($MeC{=}N$), 173.7 ($C{=}NH$), 177.2 ($HCC{=}N$). IR (cm^{-1}, Nujol): 3330 (m, ν_{NH}), 2728 (w), 2366 (vw), 2344 (vw), 2173 (m, $\nu_{C\equiv N}$), 1658 (m, $\nu_{N=C}$), 1621 (m, $\nu_{N=C}$), 1584 (m, $\nu_{N=C}$), 1301 (s), 1245 (m), 1218 (m), 1206 (m), 1187 (m), 1152 (m), 1130 (m), 1059 (m), 1030 (m), 1017 (m), 982 (m), 930 (m), 899 (m), 820 (w), 699 (s), 679 (s), 610 (m), 589 (m, ν_{GaC}), 551 (m, $\nu_{as\ GaC_2}$), 538 (m, $\nu_{s\ GaC_2}$), 505 (m), 473 (m), 457 (m, ν_{GaN}), 415 (m, ν_{GaN}), 399 (m), 359 (w), 338 (w), 305 (w), 282 (vw), 224 (w), 169 (w), 153 (w). EI-MS (m/z (relative intensity), fragment): 924 (2), $(M - MeCN - H)^+$; 453, $(M/2 - 2Me)^+$; 99 (100), $(GaMe_2)^+$; 84 (5), $(GaMe)^+$; 69 (10), Ga^+; 41 (83), $(MeCN)^+$. Anal. Calcd: C, 37.10; H, 5.40; N, 14.42. Found: C, 37.41; H, 5.49; N, 14.50.

Synthesis of 2·3MeCN. A 1.95 g (17 mmol) amount of $GaMe_3$ and 0.06 g (0.35 mmol) of CsCl were dissolved in 50 mL of MeCN. The reaction mixture was stirred at 60 °C for 75 h, filtered, and cooled to 5 °C for 2 days. **2**·3MeCN crystallizes as amber-colored prisms (0.25 g, 8% yield based on $GaMe_3$). ^1H NMR (toluene-d_8, ppm): −0.42 (s, 12 H, $Ga(CH_3)_2$), −0.36 (s, 12 H, $Ga(CH_3)_2$), −0.33 (s, 6 H, $GaCH_3$), 1.50 (s, 6 H, $H_3CC{=}NH$), 1.84 (s, 12 H, $H_3CC{=}N$), 1.92 (s, H, CH_3CN), 5.07 (s, Br, 2 H, NH), 5.95 (s, 2 H, C_3CH). ^{13}C NMR (toluene-d_8, ppm): −4.9 ($Ga(CH_3)_2$), −4.5 ($Ga(CH_3)_2$), −4.1 ($GaCH_3$), 0.4 (CH_3CN), 27.0 ($H_3CC{=}N$), 30.0 ($H_3CC{=}NH$), 68.2 (C_3CH), 77.3 ($CC{\equiv}N$), 118.1 (CH_3CN), 122.9 ($C{\equiv}N$), 162.1 ($MeC{=}N$), 173.8 ($C{=}NH$), 177.4 ($HCC{=}N$). IR (Nujol, cm^{-1}): 3319 (m, ν_{NH}), 2854 (vw), 2730 (w), 2359 (vw), 2300 (m, $\nu_{C\equiv N}$), 2245 (m, $\nu_{C\equiv N}$), 1624 (s, $\nu_{N=C}$), 1578 (s, $\nu_{N=C}$), 1561 (s, $\nu_{N=C}$), 1304 (s), 1258 (m), 1213 (m), 1203 (m), 1188 (m), 1154 (m), 1125 (m), 1050 (w), 1025 (m), 1003 (m), 972 (m), 934 (m), 868 (m), 816 (w), 764 (s), 704 (s), 689 (s), 627 (m), 586 (m, ν_{GaC}), 567 (m, $\nu_{as\ GaC_2}$), 536 (m, $\nu_{s\ GaC_2}$), 505 (m), 473 (m, ν_{GaN}), 405 (m, ν_{GaN}), 395 (m), 351 (w), 329 (m), 305 (w), 280 (vw), 226 (w), 165 (w), 147 (w). Anal. Calcd: C, 39.51; H, 5.62; N, 16.64. Found: C, 39.28; H, 5.49; N, 16.41.

Synthesis of 2·2GaMe$_3$. A 2.3 g (10.4 mmol) amount of **1**, 0.03 g (0.2 mmol) of CsF, and 1.2 g (10.5 mmol) of $GaMe_3$ were dissolved in 50 mL of MeCN. The reaction mixture was stirred at 60 °C for 24 h, filtered, and cooled to −20 °C for 2 days. **2**·2GaMe$_3$ crystallizes as amber-colored prisms (0.2 g, 10% yield based on $GaMe_3$). ^1H NMR (toluene-d_8, ppm): −0.44 (s, 12 H, $Ga(CH_3)_2$), −0.35 (s, 12 H, $Ga(CH_3)_2$), −0.29 (s, 6 H, $GaCH_3$), 0.0 (s, 18 H, $Ga(CH_3)_3$), 1.48 (s, 6 H, $H_3CC{=}NH$), 1.8 (s, 12 H, $H_3CC{=}N$), 5.0 (s, br, 2 H, NH), 5.91 (s, 2 H, C_3CH). ^{13}C NMR (toluene-d_8, ppm): −4.8 ($Ga(CH_3)_2$), −4.5 ($Ga(CH_3)_2$), −4.2 ($GaCH_3$), −2.1 ($Ga(CH_3)_3$), 27.4 ($H_3CC{=}N$), 29.9 ($H_3CC{=}N$), 68.0 (C_3CH), 77.4 ($CC{\equiv}N$), 122.0 ($C{\equiv}N$), 161.3 ($MeC{=}N$), 173.6 ($HC{=}N$), 177.9 ($HCC{=}N$). IR (Nujol, cm^{-1}): 3331 (m, ν_{NH}), 2856 (vw), 2727 (w), 2178 (m, $\nu_{C\equiv N}$), 1634 (s, $\nu_{N=C}$), 1595 (s, $\nu_{N=C}$), 1575 (s, $\nu_{N=C}$), 1299 (s), 1254 (m), 1210 (m), 1211 (m), 1181 (m), 1152 (m), 1124 (m), 1130 (m, br), 1010 (m), 976 (m), 943 (m), 860 (m), 814 (w), 759 (s), 700 (s), 687 (s), 625 (m), 588 (m, ν_{GaC}), 569 (m, $\nu_{as\ GaC_2}$), 539 (s, br, $\nu_{s\ GaC_2}$, ν_{GaC_3}), 511 (s, br, ν_{GaC_3}), 472 (m, ν_{GaN}), 400 (m, ν_{GaN}), 395 (m), 373 (m, ν_{GaNC}), 353 (w), 333 (w), 301 (w), 282 (vw), 221 (w), 165 (w), 152 (w). Anal. Calcd: C, 36.01; H, 5.88; N, 11.67. Found: C, 35.85; H, 5.70; N, 11.61.

X-ray Structure Determination of 1, 2, 2·3MeCN, and 2·2GaMe$_3$. The crystals were covered with a perfluorinated polyether and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The reflections were collected with an IPDS system (Stoe; Mo Kα radiation; $\lambda = 0.710\ 73$ Å) for **1** and **2**·2GaMe$_3$. **2** was measured with a CAD4 diffractometer (Enraf-Nonius; Cu Kα radiation; $\lambda = 1.541\ 78$ Å). For **2**·3MeCN a P4 diffractometer (Siemens; Mo Kα radiation; in all cases graphite-monochromated) was used. The intensities were corrected for Lorentz and polarization effects (for absorption correction, cell parameters, and collecting of the intensities, see Table 1). All structures were solved by direct methods (**1**, **2**, **2**·3MeCN, SHELXTL;[10] **2**·2GaMe$_3$, SHELXTL-Plus[11]) and refined against F^2 by full-matrix least squares with the program SHELXTL. The hydrogen atoms were treated as followed: free refinement in **1**; all positions of the H atoms except for the N−H functions in **2**, **2**·3MeCN, and **2**·2GaMe$_3$ were calculated for an ideal geometry and refined with a common displacement parameter. The calculation of the bond lengths, bond angles, and U$_{eq}$ values was performed using the program PLATON.[12]

Selected bond lengths and angles of **1**−**2**·2GaMe$_3$ are listed in Table 2.

Results and Discussion

The reaction of acetonitrile with AlMe$_3$ at 80 °C gives the dimer [Me$_2$Al(NCMe$_2$)]$_2$.[13] In contrast, GaMe$_3$ does not react with MeCN under these conditions but gives a weak donor−acceptor complex [Me$_3$Ga(NCMe)].[14] The situation changes when cesium salts, CsF, CsCl, and CsBr, are added to the GaMe$_3$/MeCN mixture. The solutions become dark brown, and the ^{1}H NMR spectra show the decrease of the signal of GaMe$_3$ (or the species [XGaMe$_3$]$^-$ and [X(GaMe$_3$)$_2$]$^-$ depending on the amount of CsX). The resonances due to two new compounds in the ratio of ca. 9:1 arise. At reflux and with reaction times of more than 90 h an ivory-colored polymer which is insoluble in common organic media precipitated. Further investigations showed that only a catalytic amount of cesium salt is necessary, good results being obtained with 1−2 mol % of CsF, CsCl, or CsBr.

The major product (eq 1) was isolated by flash chromatography through silanized silica gel. The minor compound can be obtained by storing the reaction mixture at −25 °C. [(Me$_2$Ga)$_4$(MeGa)$_2${HNC(Me)C(CN)-CH(NCMe)$_2$}$_2$] (**2**) crystallizes as amber prisms. The formation can be rationalized according eq 2. **2** was crystallized in two other forms, depending on the

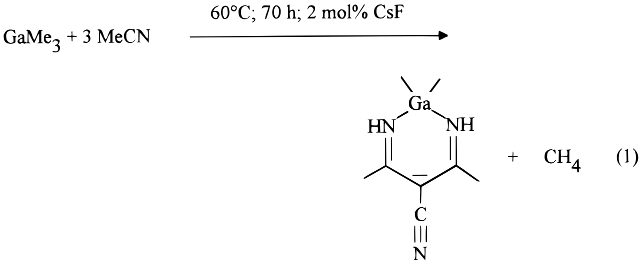

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Table 2. Selected Bond Lengths (pm) and Angles (deg) of 1, 2, 2·3MeCN, and 2·2GaMe$_3$

	Compound **1**		
Ga1−N1	195.7(2)	C2−C3	150.5(4)
Ga1−N3	196.9(2)	C2−C4	142.8(3)
Ga1−C1	196.3(2)	C4−C5	142.0(3)
N1−C2	129.7(3)	C4−C6	140.7(3)
N2−C5	115.1(3)	C6−C7	150.7(4)
N3−C6	130.7(3)		
N1−Ga1−N3	90.95(9)	C3−C2−C4	118.7(2)
N1−Ga1−C1	110.92(9)	C2−C4−C5	116.3(2)
N3−Ga1−C1	110.17(9)	C2−C4−C6	126.3(2)
C1−Ga1−C1a	119.9(1)	C5−C4−C6	117.3(2)
Ga1−N1−C2	128.7(2)	N2−C5−C4	178.7(3)
Ga1−N3−C6	128.5(2)	N3−C6−C4	122.7(2)
N1−C2−C3	118.5(2)	N3−C6−C7	118.5(2)
N1−C2−C4	122.8(2)	C4−C6−C7	118.8(2)
	Compound **2**		
Ga1−N1	196.9(8)	N3−C7	128(1)
Ga1−N2	197.7(7)	N4−C14	131(1)
Ga1−N3	192.9(8)	N5−C13	114(1)
Ga2−N1	200.5(8)	C6−C7	154(1)
Ga2−N2a	200.4(7)	C6−C2	151(1)
Ga3−N3	197.5(8)	C6−C4	154(1)
Ga3−N4	196.9(9)	C12−C7	146(1)
N1−C2	129(1)	C12−C13	143(2)
N2−C4	128(1)	C12−C14	142(2)
N1−Ga1−N2	93.0(3)	C13−C12−C14	116.8(9)
N2−Ga1−N3	96.8(3)	C7−C12−C14	124.7(9)
N1−Ga1−N3	96.1(3)	C6−C7−C12	117.3(8)
N1−Ga2−N2a	90.1(3)	C6−C7−N3	117.0(9)
N3−Ga3−N4	93.1(4)	N3−C7−C12	125.7(9)
Ga1−N1−C2	109.1(7)	C12−C14−C15	118.4(9)
Ga1−N1−Ga2	120.2(4)	C12−C14−N4	123(1)
Ga2−N1−C2	130.6(7)	N4−C14−C15	118(1)
Ga2a−N2−Ga1	119.3(4)	C2−C6−C7	109.9(8)
Ga2a−N2−C4	130.2(7)	C4−C6−C7	109.1(8)
Ga1−N2−C4	110.6(7)	C2−C6−C4	110.4(8)
Ga1−N3−Ga3	120.8(4)	N1−C2−C3	124.2(9)
Ga1−N3−C7	113.7(7)	N1−C2−C6	121.2(9)
Ga3−N3−C7	125.4(7)	C3−C2−C6	114.6(9)
Ga3−N4−C14	127.4(8)	N2−C4−C6	119.5(8)
C12−C13−N5	177(1)	N2−C4−C5	126(1)
C13−C12−C7	118.4(9)	C5−C4−C6	115.0(9)
	Compound **2**·3MeCN		
Ga1−N1	195.3(9)	Ga4−N7	198.4(9)
Ga1−N2	198(1)	Ga4−N8	192(1)
Ga1−N3	196.0(9)	Ga4−C16	192(1)
Ga2−N1	201.3(9)	Ga5−N6	200(1)
Ga2−N2a	200(1)	Ga5−N7a	201(1)
Ga3−N3	195(1)	Ga6−N8	193.6(9)
Ga3−N4	195(1)	Ga6−N9	195(1)
C12−C7	144(1)	C27−C29	142(2)
C12−C13	143(2)	C27−C22	142(2)
C12−C14	145(2)	C27−C28	142(2)
C13−N5	115(2)	C28−N10	113(2)
Ga4−N6	191.5(9)		
N1−Ga1−N2	93.8(4)	N6−Ga4−N7	94.2(4)
N1−Ga1−N3	96.8(4)	N6−Ga4−N8	97.7(4)
N2−Ga1−N3	97.2(4)	N7−Ga4−N8	96.0(4)
N1−Ga2−N2a	89.4(4)	N6−Ga5−N7a	88.5(4)
N3−Ga3−N4	91.7(5)	N8−Ga6−N9	93.8(4)
C7−C12−C13	119(1)	C22−C27−C28	119(1)
C7−C12−C14	124(1)	C22−C27−C29	126(1)
C13−C12−C14	117(1)	C28−C27−C29	119(1)
C12−C13−N5	178(1)	C27−C25−N10	178(2)
	Compound **2**·2GaMe$_3$		
Ga1−N1	197.4(4)	Ga3−N4	197.4(5)
Ga1−N2	197.9(4)	Ga4−N5	214.7(4)
Ga1−N3	194.1(4)	C12−C7	145.0(5)
Ga2−N2	202.8(4)	C12−C13	141.2(6)
Ga2−N1a	202.9(4)	C13−N5	114.9(6)
Ga3−N3	196.6(4)	C12−C14	142.9(6)
N1−Ga1−N2	93.0(2)	Ga4−N5−C13	142.2(4)
N1−Ga1−N3	96.4(2)	C7−C12−C13	119.4(4)
N2−Ga1−N3	96.2(2)	C7−C12−C14	124.6(4)
N2−Ga2−N1a	89.7(2)	C13−C12−C14	115.8(4)
N3−Ga3−N4	91.7(2)	C12−C13−N5	179.4(6)

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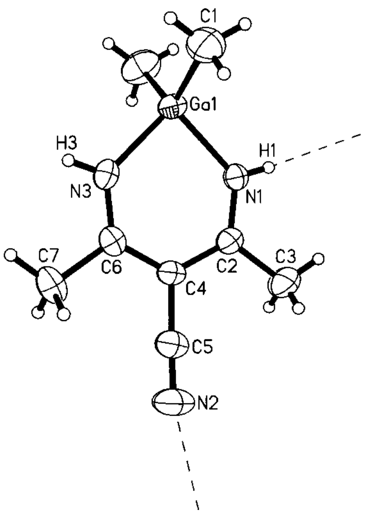
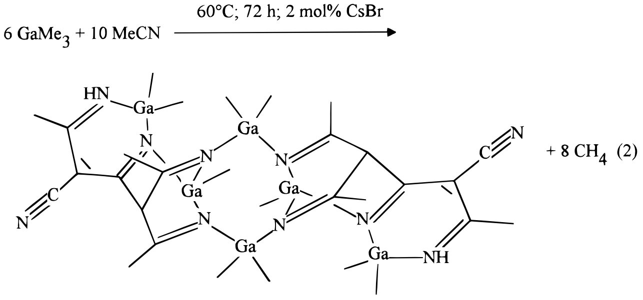


Figure 1. Graphical representation of **1** (ellipsoids with 50% probability level).

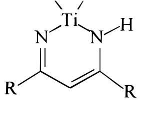
remaining starting materials MeCN and $GaMe_3$, **2**·3MeCN and **2**·2$GaMe_3$, respectively.



2

The starting point of the formation of **1** and **2** very likely is the initial formation of triorganohalogeno metalates, $[Me_3GaX]^-$, which are more basic than $GaMe_3$ and are therefore able to deprotonate acetonitrile under mild conditions because of the weakening of the Ga−C bond. During the reaction the intermediates probably are already coordinated to the Me_2Ga fragment, because the catalytic reaction of nitriles with a free base in absence of a strong Lewis acid leads to the well-known trimerization to 1,3,5-triazines.[15]

Molecules similar to **1** are known in transition metal chemistry. Cp_2TiMe_2 and related compounds react with two molecules of a nitrile to form a six-membered heterocycle such as



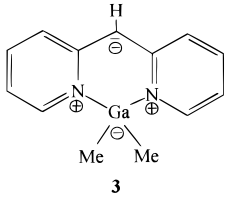
via a metal carbene intermediate.[16,17]

1, shown in eq 1 in its resonance form, can be described as a double betaine. However, it is obvious that the formal charge on C4 is delocalized over the N−C skeleton. A similar behavior is found for the six-membered ring fragments in **2**. Compound **1** is a colorless air-stable compound with an unpleasant, moldy smell, which can be hydrolyzed to the corresponding metal-free iminium salt with 1 M hydrochloric acid.

The IR spectrum of **1** shows two NH absorptions at 3352 and 3258 cm^{-1}, due to the hydrogen bridge of one of the iminium functions to a nitrile group of a adjacent molecule. Therefore, the absorption at 3258 cm^{-1} is broadened. The band for the nitrile function is found at 2199 cm^{-1}. The bands at 1600, 459, and 410 cm^{-1} are characteristic for $\nu_{N=C}$, $\nu_{as\ GaN}$, and $\nu_{s\ GaN}$, respectively.[18] To furnish proof for the origin of the H atoms at the iminium functions, the reaction to **1** was examined with CD_3CN. **1**-d_8 could be isolated and characterized by NMR and IR spectroscopy. The ν_{ND} bands were observed at 2484 and 2408 cm^{-1}. Therefore, it is clear that the H atoms of the NH groups in **1** were delivered by acetonitrile and not by H_2O impurities. In CH_2Cl_2 solution the H bridges are cleaved and one sharp band at 3359 cm^{-1} results. The ν_{NH} band at 3330 cm^{-1} in **2** is sharp as well as the $\nu_{C\equiv N}$ absorption at 2172 cm^{-1}. The different C=N groups in **2** result in bands at 1658, 1621, and 1584 cm^{-1}. The vibrations at 505, 473, 457, and 415 cm^{-1} were assigned to the GaN bonds. The absorptions at 565 and 543 cm^{-1} in **1** as well as 589, 551, and 538 cm^{-1} in **2** are the values for the Ga−C vibrations.[18] The insoluble polymer, obtained by further heating of **1** and **2** in MeCN/$GaMe_3$ mixtures, shows the typical vibrations already found for **2**, e.g., 3349 and 3309 cm^{-1} (ν_{NH}) and 2173 cm^{-1} ($\nu_{C\equiv N}$) as well as 1622, 1577, and 1531 cm^{-1} ($\nu_{C=N}$). Therefore, one can assume that the polymer is formed by a condensation reaction of **2** with further MeCN and $GaMe_3$ units.

The ^1H NMR spectrum of **1** in toluene-d_8 shows one resonance at −0.2 ppm for the Me_2Ga fragment, one signal at 5.24 ppm for the NH groups, and two signals at 1.66 and 1.67 ppm for the MeC=N groups. This is a hint at weak NH···N≡C contacts which discriminate the two NH groups. Nevertheless, the cryoscopic measurements of **1** in benzene yield a monomeric molecular weight. The hexanuclear complex **2** in toluene-d_8 exhibits three lines at −0.41, −0.34, and −0.32 ppm for the four Me_2Ga and the two MeGa fragments, respectively. **2**·2$GaMe_3$ gives one more signal at 0.0 ppm for the $GaMe_3$ moieties. The methine-H atom shows a resonance at 5.95 ppm.

In the ^{13}C NMR spectra of **1** the differentiation of the two MeC=N groups was not observed, with only one signal at 27.5 ppm. The line for the resonance-stabilized carbanionic C atom was found at 78.7 ppm; 88.0 ppm is the corresponding signal in $[Me_2Ga(2\text{-}NC_5H_4)_2CH]$ (**3**).[19] The nitrile and the iminium C atoms show values



3

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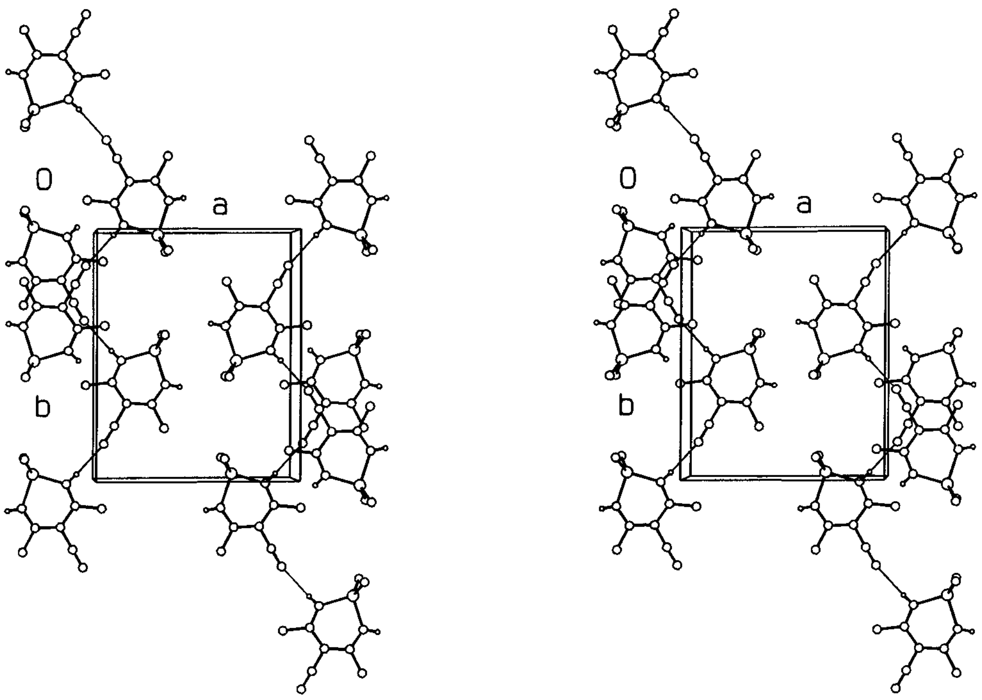

Figure 2. Stereoscopic view of the unit cell of **1**. The zigzag arrangement through H bridges runs along [010].

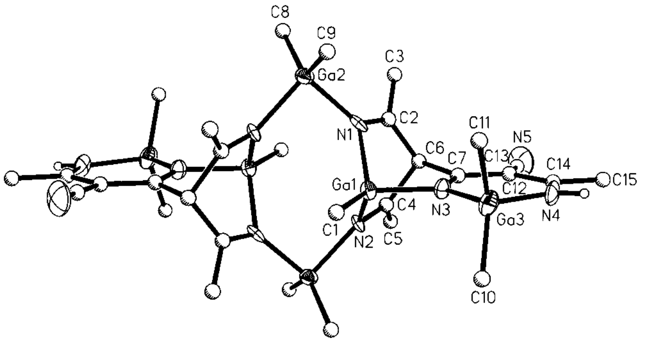

Figure 3. Plot of the centrosymmetric molecule **2** (C atoms represented as spheres; without H atoms except NH functions).

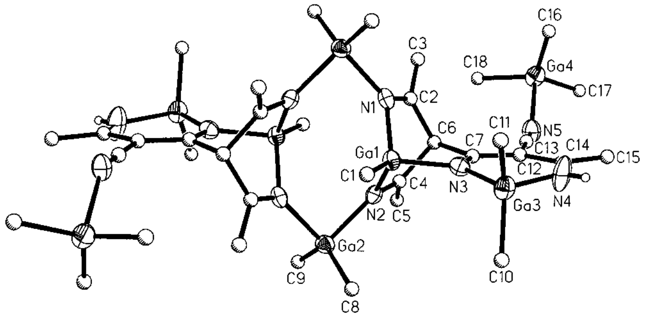

Figure 5. Plot of the centrosymmetric molecule **2**·2GaMe$_3$.

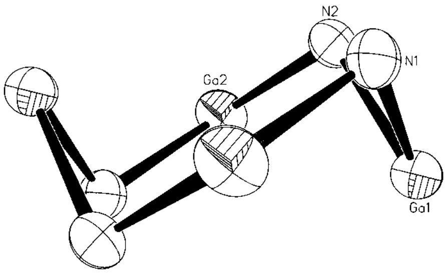

Figure 6. Illustration of the eight-membered Ga$_4$N$_4$ ring in **2**·2GaMe$_3$.

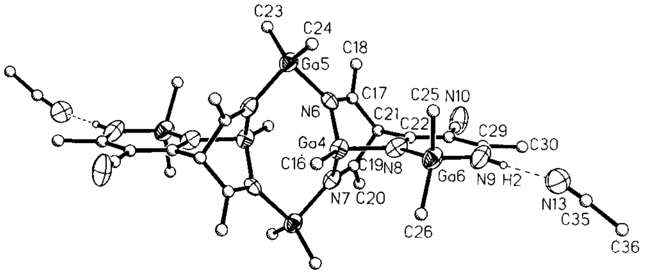

Figure 4. Plot of the centrosymmetric molecule of **2**·3MeCN forming H bridges to two acetonitrile molecules.

of 121.5 and 173.5 ppm, respectively. As can be expected from the graphic representation of **2**, the structure elements C=N should cause three signals (161.6, 173.7, 177.2 ppm). The Me$_2$Ga and MeGa fragments are responsible for three signals at −4.7, −4.5, and −4.2 ppm. **2**·2GaMe$_3$ possesses in addition to **2** a resonance at −2.1 ppm for the coordinated GaMe$_3$ unit. The value for the methine C atom was determined to 68.2 ppm.

The EI mass spectrum of **1** shows the molecular peak of $m/z = 221$ with low intensity, while in the spectrum of **2** the highest observed fragment belongs to $(M - MeCN - H)^+$ ($m/z = 924$). The spectrum of the polymer is almost identical with that of **2**.

Figure 1 gives a graphical representation of a molecule of **1**. The heterocycle can be formally divided into a GaMe$_2$ fragment and the organic ligand {HNC(Me)}$_2$C(CN), an acetylacetonate derivative. One iminium function participates in the formation of hydrogen bridges to a nitrile group of an adjacent molecule (N1···N2a 302.9 pm). The hydrogen bridges lead to a zizag arrangement in the unit cell pointing along the *b*-axis (Figure 2). The negative charge is delocalized over the NC skeleton, indicated by the distances N1−C2 129.7(3), N3−C6 130.7(3), C2−C4 142.8(3), C4−C6 140.7(3), and C4−C5 142.0(3) pm. Therefore, the planarity of the six-membered ring is not surprising. The entire skeleton except C1 lies on a crystallographic mirror plane. The comparable C−C bond lengths in **3** are 138.8(5) and 140.3(5) pm.[19]

The six-membered heterocycle also is an important feature for the hexanuclear complexes **2** (Figure 3), **2**·3MeCN (Figure 4), and **2**·2$GaMe_3$ (Figure 5). The basic C−C and C−N distances there are quite similar to the values in **1**. The Ga−N bond lengths in the four complexes cover a range of 194−203 pm, comparable with the values found in **3** (198.3(3), 197.9(3) pm), $[Me_2GaNCMe_2]_2$ (197.8(3), 200.0(3) pm),[20] $[Me_2GaN(H)t\text{-}Bu]_2$ (201.2(4) pm),[21] and $[(PhCH_2)_2GaN(H)t\text{-}Bu]_2$ (202.0(5), 201.3(4) pm).[22] An exception to this is the long donor−acceptor bond Ga4−N5 of 214.7(4) pm in **2**·2$GaMe_3$ causing only a weak pyramidalizing of the GaC_3 unit (angular sum: 351°). An analogous geometry was found for $[Mes_3Ga(NCMe)]$.[6]

The structure of **2**·3MeCN contains two crystallographic independent centrosymmetric complexes **2**. Only one molecule is involved in the formation of weak hydrogen bridges between NH functions and MeCN units with a distance N9···N13 of 312(1) pm. The centrosymmetric eight-membered rings of **2**−**2**·2$GaMe_3$ are strongly puckered and almost identical in their geometry. An example is given in Figure 6. This ring from **2**·2$GaMe_3$ consists of three planes, a center plane built up by two gallium and four nitrogen atoms (mean deviation from plane: 4 pm) and two GaN_2 planes. The angle enclosed by the center plane and the peripheric plane is 85°.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and isotropic or anisotropic displacement parameters for all atoms in **1**, **2**, **2**·3MeCN, and **2**·2$GaMe_3$ (28 pages). Ordering information is given on any current masthead page.

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