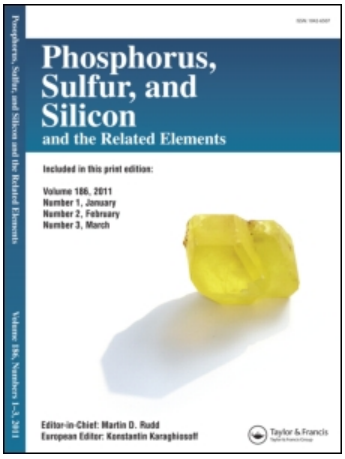

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SYNTHESIS AND STRUCTURES OF NEW AMINOGALLANES WITH FOUR AND SIX MEMBERED RINGS: A NOVEL THERMOLYSIS REACTION OF THE DIAZASILAGALLETIDINE $[Me_2Si(NtBu)_2GaCl]_2$

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SYNTHESIS AND STRUCTURES OF NEW AMINOGALLANES WITH FOUR AND SIX MEMBERED RINGS: A NOVEL THERMOLYSIS REACTION OF THE DIAZASILAGALLETIDINE $[Me_2Si(NtBu)_2GaCl]_2$

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

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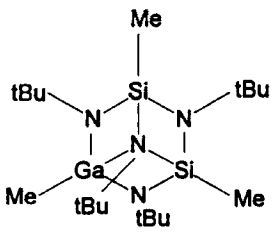
The dimeric diazasilagalletidines, $[Me_2Si(NtBu)_2GaX]_2$, X = Me (**1**) and Cl (**2**), were synthesized by the reaction of gallium trichloride with the dilithiated salt of bis(*t*-butylamino)dimethylsilane or with the diazasilastannetidine $Me_2Si(NtBu)_2Sn$, respectively. By the latter method, the polycycle $(MeSi)_2(NtBu)_4(GaCl)$ (**3**) was obtained as a by-product; compound **3** is also formed by thermolysis of **2** in vacuum. The molecular structures of **1**–**3** have been determined by X-ray methods. Compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$; compound **3** is isotypic to the previously known $(MeSi)_2(NtBu)_4GaMe$ and the structure was solved in the space group $P2_1/c$. Other crystallographic data: **1**, a = 11.240(6) Å, b = 8.668(4) Å, c = 15.702(8) Å, β = 100.83(3)°, Z = 2, V = 1502.7(13) Å^3, R = 0.052. **2**, a = 9.147(5) Å, b = 18.225(9) Å, c = 9.209(5) Å, β = 107.08(4)°, Z = 2, V = 1467.4(13) Å^3, R = 0.058. **3** a = 9.324(9) Å, b = 14.822(15) Å, c = 19.60(2) Å, β = 110.03(7)°, Z = 4, V = 2545(4) Å^3, R = 0.066. In compounds **1** and **2**, a four-membered Ga_2N_2 cycle forms the central ring to which two equal four-membered Si-N-Ga-N rings are fused in a *trans* orientation with respect to each other. The room temperature (20°C) ^{1}H NMR spectrum of compound **3** exhibits only two *t*-butyl signals of equal intensity indicating a fast intramolecular exchange process which is inhibited only at temperatures below −90°C (toluene). A tris(amino)gallane $(Me_2Si)(NtBu)_2Ga[N(SiMe_3)_2]$ (**4**) can be obtained by reaction of **2** with lithium-bis(trimethylsilyl)amide.

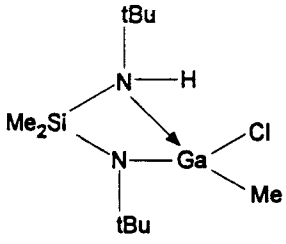
Key words: Aminogallanes, diazasilagalletidine, thermolysis, X-ray structures.

INTRODUCTION

In exploring the chemistry of gallium amides,[1–7] the diffunctional aminosilanes $Me_2Si[NH(tBu)]_2$ and $[MeSi(NHtBu)NtBu]_2$ as well as the (alkoxy)aminosilane $Me_2Si(OtBu)[NH(tBu)]$ have been successfully employed in our earlier studies. In this context we have previously explored the reaction of gallium trichloride with $Me_2Si[N(tBu)Li]_2$,[4,8] in toluene/hexane medium in an effort to obtain the derivative $[ClGa(NtBu)_2SiMe_2]_2$; however, the 1:1 stoichiometric reaction afforded the cage compound $(MeSi)_2(NtBu)_4GaMe$ (**A**) in 20% yield (based on gallium trichloride used).[4] As a side product, likely due to incomplete lithiation, the compound $Me_2Si[NH(tBu)((NtBu)GaCl(Me)]$ (**B**) was also isolated (≈5%). It is thus apparent that other gallium products could perhaps be obtained by altering the reaction



A

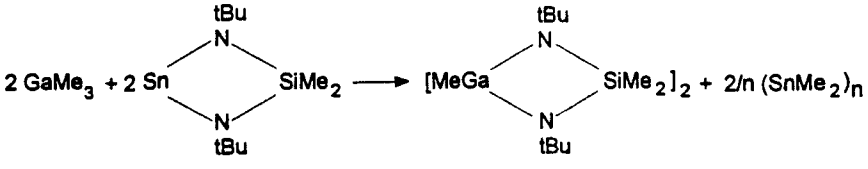


B

SCHEME I

conditions which is what we intended to probe further in the current study. Exchange of Ga—Cl bond by Si—C bond is an additional feature of interest[8] that could have precluded the formation of the expected product.

In a somewhat related study, the reaction of trimethylgallium with the diazasilastannetidine $Me_2Si(NtBu)_2Sn$ was conducted in order to accomplish the synthesis and isolation of the methyl derivative $[MeGa(NtBu)_2SiMe_2]_2$ (Equation 1).[1]



(1)

1

Although the corresponding reaction with both trimethylaluminium and trimethylindium afforded pure products the gallium compound could not be isolated. This compound, however, was observed in the mass spectrum of $Me_2Si[(NtBu)GaMe_2]_2$.

In this paper we report syntheses and X-ray structures of both $[Me_2Si(NtBu)_2GaMe]_2$ (**1**) and $[Me_2Si(NtBu)_2GaCl]_2$ (**2**). We also describe the X-ray structure for the chloro cage compound $(MeSi)_2(NtBu)_4GaCl$[7] the synthesis of which was accomplished by a new route involving the thermolysis of **2**. Compound **2** can be a synthetically useful precursor for other gallium derivatives as illustrated here by the synthesis of the tris(amino)gallane, $Me_2Si(NtBu)_2Ga(N(SiMe_3)_2)$ (**4**). The synthetic routes to these aminogallanes involve the use of the diazasilastannetidine $Me_2Si(NtBu)_2Sn$ or of the lithiated aminosilanes and differ from the dehalosilylation of silylamines used by Nutt and coworkers to obtain dihalogenoaminogallanes of type $[X_2GaN(R)(SiMe_3)]_n$.[9]

RESULTS AND DISCUSSION

Synthesis

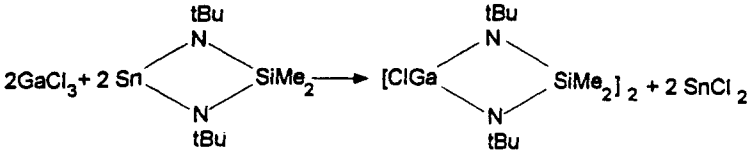
At the outset, our objective was to synthesize **2**, if possible, by the route given in Equation (2) by altering the reaction conditions.[4] As noted in the introduction, by

using a toluene/hexane medium, the compound $(MeGa)(NtBu)_4(SiMe)_2$ (**A**) was obtained before.[4] Changing the reaction solvent to diethyl ether/hexane in the present work did alter the products and (**A**) was not found (^1H NMR). A large number of peaks were observed in the ^1H NMR spectrum of the reaction mixture with the exclusion of those ascribable to the desired compound **2**. Sublimation of the solid reaction mixture afforded $Me_2Si(NtBu)_2GaMe$ (**1**) in low but significant yields. Thus it is apparent that the nature of the products formed in the reaction of gallium trichloride with the dilithiated reagent is solvent dependent.

$$2GaCl_3 + 2(LiNtBu)_2SiMe_2 \rightarrow [ClGa(NtBu)_2SiMe_2]_2 + 4LiCl \qquad (2)$$

In the formation of both **A** and **1** an exchange of methyl groups between Ga—Cl and Si—Me had occurred, a feature which we have noted before.[2,8] In contrast, in the reaction of trimethylsilyl substituted amines with gallium trichloride, no such exchange has been reported.[9] Another relevant observation is that a reaction of the chloro derivative **2** with half mole equivalent of $(LiNtBu)_2SiMe_2$ resulted in obtaining a solid product in which **1** and **2** had co-crystallized.[10] Thus one possible pathway for the formation of **1** is the methyl exchange reaction of initially formed **2** with $(LiNtBu)_2SiMe_2$.[11]

Use of the stannylene $Sn[(NtBu)_2SiMe_2]$ in place of the dilithiated silylamide readily affords **2** in modest yields (Equation 3).

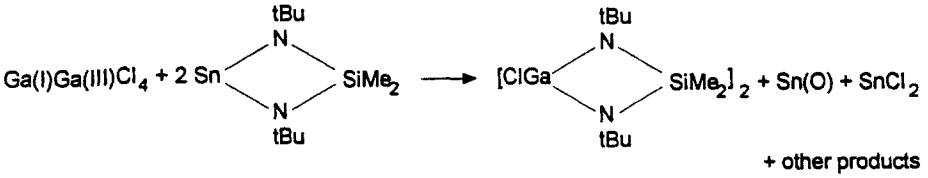


(3)

2

We have previously used the above stannylene for the synthesis of $E[NtBu)_2SiMe_2]$ where E = Mg, (Cl)As or (Cl)Sb.[12] For the gallium compound **2**, changing the reaction medium (diethylether, benzene, toluene) did not appreciably affect the yield; the compound readily crystallizes out upon concentrating the filtrate and cooling.

Compound **2** is also a major product in the reaction of $GaCl_2$ [or $Ga(I)Ga(III)Cl_4$] with $Me_2Si(NtBu)_2Sn$ (Equation 4).



(4)

2

Although the method is interesting, it involves an additional step of preparing $GaCl_2$ as well as difficulty in filtration which precludes its utility for the synthesis of pure **2**.

In an attempt to maximize the yield of **2** the precipitate obtained in the reaction (amount greater than that expected for $SnCl_2$), after extracting the soluble part

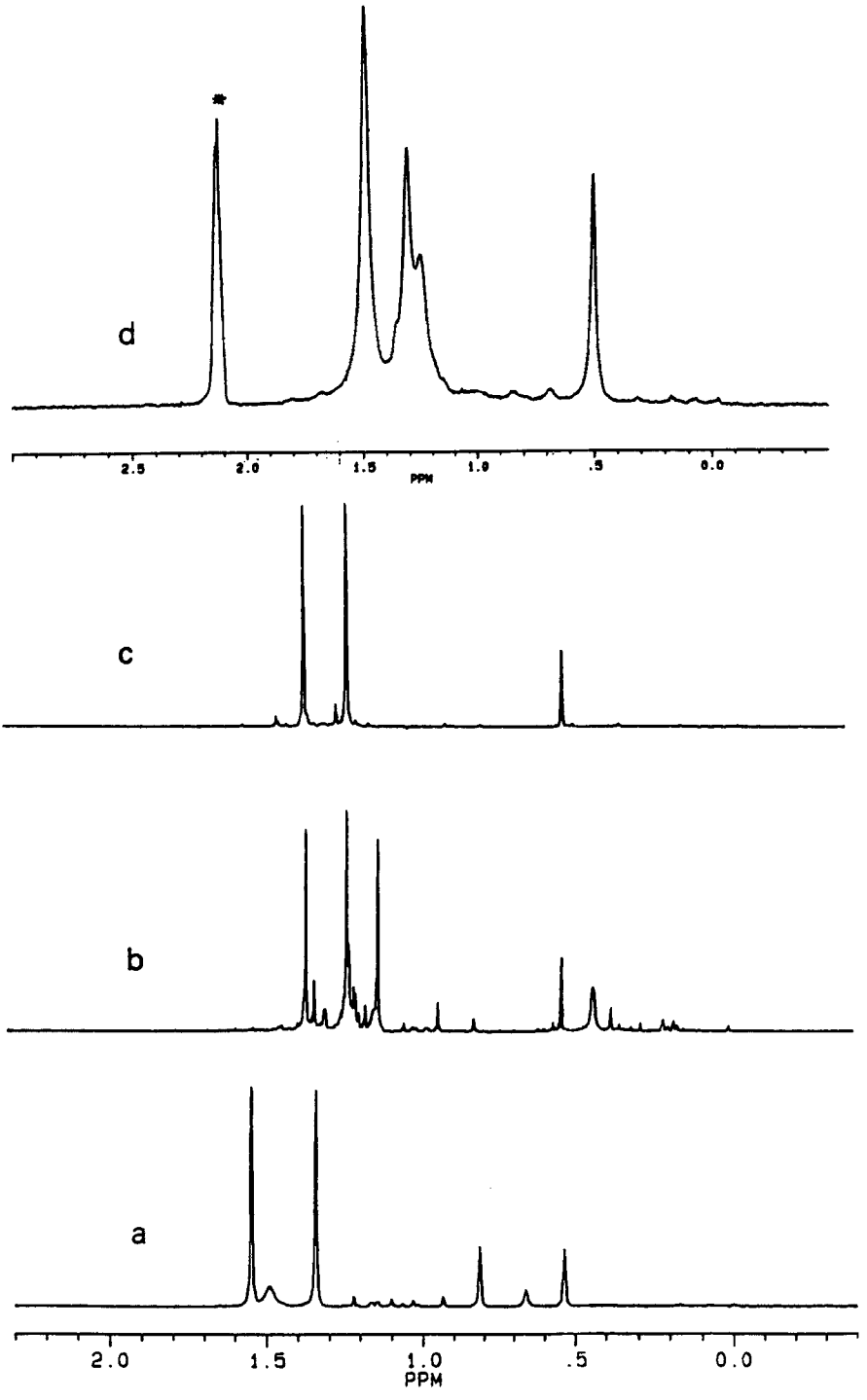


FIGURE 1 The ^{1}H NMR spectra of (a) compound **2** (b) sublimate obtained after heating **2** in vacuum (c) compound **3** at 20°C and (d) compound **3** at −95°C. Spectra (a)–(c) are in benzene-d_6 and (d) is in toluene-d_8. The peak marked by "*" in (d) is due to toluene-d_8.

with toluene, was sublimed *in vacuo*. Surprisingly, under these conditions we could isolate a second compound **3** *albeit* in low yields. Compound **3** is also formed in a novel thermal reaction when **2** is heated *in vacuo* (Figure 1). Thus it is likely that a part of **2** is occluded with tin(II)chloride (cf Equation 2) and upon sublimation, transformed to **3**. The ^{1}H NMR spectra for **2**, the sublimate and **3** are shown in Figure 1 (discussed below). As yet we have not been able to identify the other products in this thermolysis. Thus it can only be noted that theoretically **3** can result from **2** by eliminating one equivalent of chlorodimethylgallium.

The chloro compound **2** can be used to synthesize the tris(amino)gallane **4** in a straightforward reaction (Equation 5); **4** can be isolated by crystallization in good yields.

$$1/2[Me_2Si(NtBu)_2GaCl]_2 + LiN(SiMe_3)_2 \rightarrow LiCl + \underset{\mathbf{4}}{Me_2Si(NtBu)_2GaN(SiMe_3)_2} \quad (5)$$

In the mass spectrum of **4** only the simple molecular ion peak consistent with a monomer in the gas phase is found. This finding also reflects the relatively high volatility of **4** (100°C/0.01 Torr) compared to the dimeric **1** (130°C/0.01 Torr).

^{1}*H NMR Spectra*

The proton NMR spectrum of **1** shows only one resonance each for Ga-(*Me*), Si-(*Me*) and C-(*Me*) groups whereas **2** exhibits predominantly two resonances each for Si-*Me* and C-*Me* groups. Solid state structures show nearly identical dimers for both compounds except that the Ga—N bondlengths in Ga_2N_2 rings are slightly longer for **1** [av. = 2.064 Å] when compared to **2** [av. = 2.050 Å]. Since in solution, dimer $\rightleftarrows$ monomer equilibria or an alternative intramolecular rearrangement within the dimers are possible, it may be expected that for **2** the interconversion is less facile than for **1**, leading to the observed spectral pattern. It is pertinent at this point to note that the aluminium analogue of **1** gives two resonances each whereas the indium analogue shows only one resonance each for the Si—*Me* and C—*Me* groups[1,13,14] despite the fact that cryoscopic molecular weight measurements for both showed dimeric formulation. The findings parallel well with increasing Lewis acidity at the Al-/Ga-/In-centers, which may be arranged in the following order: In-Me < Ga-Me < Ga-Cl < Al-Me.

The ^{1}H NMR spectrum of **2** (toluene-d_8) at low temperature (< −10°C) showed signals attributable to only the static dimer [1.56 and 1.37 (C-*Me*), 0.82 and 0.55 ppm (Si-*Me*)]. Upon increasing the temperature two more resonances at 1.52 (C-*Me*) and 0.72 ppm appear, become sharp at *ca* 30°C [6–8% in intensity of the major signals, see Figure 1(a) for the spectrum in benzene-d_6], and then onwards all the signals tend to become broader. We were unable to observe the coalesced signals even at +100°C to arrive at any definite proposition for the observed NMR behaviour.[15]

The room temperature ^{1}H NMR spectrum of **3** shows only two signals of equal intensity for C-*Me* protons [1.40, 1.28 ppm] and is analogous to those reported previously for $(MeSi)_2(NtBu)_4E$ [E = (Me)Ga, (Me)In or Sn].[6]

These findings are in accord with a quick exchange of nitrogen atoms serving as base systems at the gallium acidic center (see structure determination and reference[6] for further discussion).

Consequently the low temperature ^{1}H NMR spectrum of **3** shows the broadening of the upfield C-*Me* signal [1.28 ppm] and at −95°C it is partially split into mainly two signals [1.25 and 1.31 ppm, Figure 1(d)]. Thus, it is apparent that an exchange is taking place in solution. Since the signal at 1.40 ppm does not change significantly with temperature, it can be attributed to the hydrogen atoms of two of the non-exchanging N*t*Bu groups. The upfield signal [1.28 ppm, 20°C] is then ascribed to the hydrogen atoms of two exchanging N*t*Bu groups.

The ^{1}H NMR spectrum of **4** gives single resonances each for the protons of SiMe_3, SiM_2 and *t*Bu groups consistent with either a monomer or a monomer/oligomer exchanging system. So far we could not obtain a molecular mass determination in solution because of solubility problems.

TABLE I

Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
mol. formula	$C_{22}H_{54}Ga_2N_4Si_2$	$C_{20}H_{48}Cl_2Ga_2N_4Si_2$	$C_{18}H_{42}ClGaN_4Si_2$
fw	570.31	611.15	475.91
Cryst dimens, mm	0.3 x 0.4 x 0.4	0.3 x 0.35 x 0.2	0.25 x 0.4 x 0.4
Cryst color	colorless	colorless	colorless
Cryst syst.	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	11.240(6)	9.147(5)	9.324(9)
b, Å	8.668(4)	18.225(9)	14.822(15)
c, Å	15.702(8)	9.209(5)	19.60(2)
β, deg	100.83(3)	107.08(4)	110.03(7)
V, Å^3	1502.7(13)	1467.4(13)	2545(4)
Z	2	2	4
d, g cm^{-3}	1.26	1.383	1.242
no. of indep. data	2402	1618	2901
no. of data with $F_o > 2\sigma F_o$	1964	1618	2575
no. of variables	119	115	208
μ, cm^{-1}	18.9	21.1	12.4
$R(F_o)$	0.052	0.058	0.066
$R_w(F_o)$	0.044	0.058	0.066

X-Ray Structures

Table I combines most of the data available from the X-ray investigations on **1**, **2** and **3**. All structures have been solved by direct methods and refined using anisotropic temperature factors for all elements except for hydrogen atoms.[16] The hydrogen atoms have been added to the carbon atoms (tetrahedral coordination and C—H = 0.96 Å). All data as well as the F_0/F_c tables have been deposited.[17]

As all structural types are already known in principle[6,7,12] we give a very short description of the structures. Both compounds **1** and **2** crystallize in the monoclinic space group $P2_1n$, but are not isomorphous. They both use van-der-Waal's interactions in the crystal and the dimers are situated on the inversion centers of the space group (point-symmetry of the molecules C_i). In Figure 2 the two molecules are shown adjacent to each other.

From an inspection of the Figure it is obvious that the two compounds are structurally very similar. There is a nearly square central Ga_2N_2 ring to which two GaN_2Si rings are attached in *trans* orientation to one another. As expected the Ga—N distances in **1** are longer than in **2** (**1**: 2.64 versus **2**: 2.50 Å), chlorine withdrawing the electron density from gallium more than the methyl group and thus inducing a higher positive charge at the gallium atom.

The three condensed four membered rings have also been found in a similar way in the dimeric forms of $[Me_2Si(NtBu)_2Sn]_2$, $[Me_2Si(NtBu)_2In\text{-}Me]_2$ and $[Me_2Si(NtBu)_2Mg\text{-}THF]_2$.[12] In Table IV the most important bond lengths and angles are assembled and may be compared to one another. As we have stated before,[12] there is a dependence of the angle ω and the a/b relation with respect to the group electronegativity of the group MX, which is inserted in the $Me_2Si(NtBu)_2MX$ cycle. The numbers found for **1** and **2** fit well in the established series and have an almost identical a/b value compared to $Me_2Si(NtBu)_2In\text{-}Me$ (see Table IV).

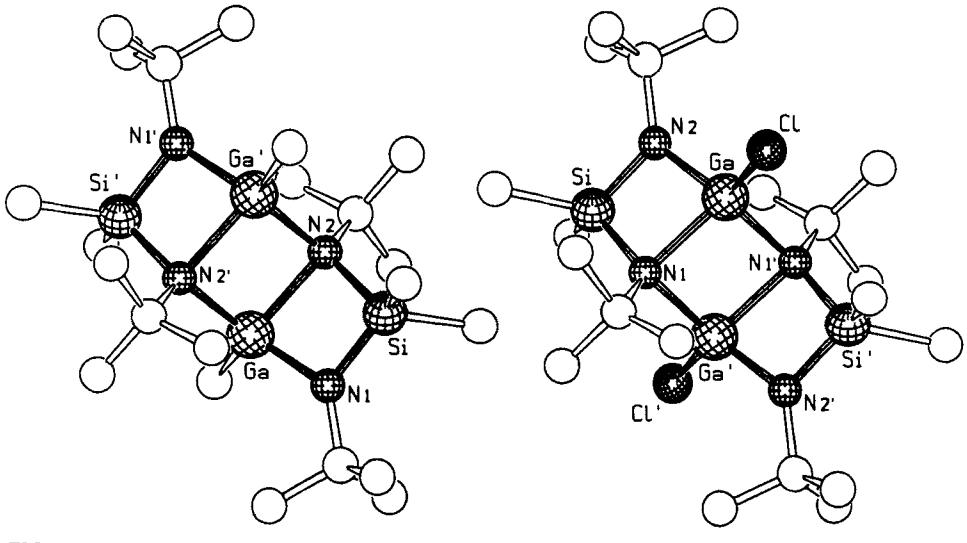


FIGURE 2 Graphic representation of the molecular structures of **1** and **2**. The carbon atoms are not labeled.

TABLE II

Bond lengths and bond angles in **1** and **2** (A represents symmetry $-x, -y, -z$)

Bond Lengths (Å) for 1

Ga–Si	2.706	(2)	Ga–N(1)	1.898	(5)
Ga–N(2)	2.070	(4)	Ga–C(1)	1.985	(7)
Ga–N(2A)	2.060	(5)	Si–N(1)	1.699	(4)
Si–N(2)	1.819	(5)	Si–C(2)	1.881	(7)
Si–C(3)	1.889	(7)	N(1)–C(8)	1.490	(8)
N(2)–C(4)	1.532	(7)	C(4)–C(5)	1.532	(8)
C(4)–C(6)	1.518	(10)	C(4)–C(7)	1.541	(10)
C(8)–C(9)	1.513	(11)	C(8)–C(10)	1.527	(11)
C(8)–C(11)	1.517	(9)			

Bond Angles (°) for 1

N(1)–Ga–N(2)	80.7(2)	N(1)–Ga–C(1)	115.1(3)
N(2)–Ga–C(1)	127.9(2)	N(1)–Ga–N(2A)	116.5(2)
N(2)–Ga–N(2A)	89.0(2)	C(1)–Ga–N(2A)	120.0(3)
N(1)–Si–N(2)	93.9(2)	N(1)–Si–C(2)	116.3(3)
N(2)–Si–C(2)	112.7(3)	N(1)–Si–C(3)	115.9(3)
N(2)–Si–C(3)	119.3(3)	C(2)–Si–C(3)	99.9(3)
Ga–N(1)–Si	97.4(2)	Ga–N(1)–C(8)	131.4(4)
Si–N(1)–C(8)	130.4(4)	Ga–N(2)–Si	87.9(2)
Ga–N(2)–C(4)	120.8(3)	Si–N(2)–C(4)	118.0(4)
Ga–N(2)–GaA	91.0(2)	Si–N(2)–GaA	114.5(2)
C(4)–N(2)–GaA	118.0(3)	N(2)–C(4)–C(5)	107.9(5)
N(2)–C(4)–C(6)	112.8(5)	C(5)–C(4)–C(6)	110.8(5)
N(2)–C(4)–C(7)	110.5(5)	C(5)–C(4)–C(7)	109.1(5)
C(6)–C(4)–C(7)	105.8(5)	N(1)–C(8)–C(9)	109.9(5)
N(1)–C(8)–C(10)	109.8(5)	C(9)–C(8)–C(10)	109.2(6)
N(1)–C(8)–C(11)	110.2(6)	C(9)–C(8)–C(11)	109.3(6)
C(10)–C(8)–C(11)	108.3(6)		

Bond Lengths (Å) for 2

Ga–Cl	2.166	(3)	Ga–N(1)	2.054	(7)
Ga–N(2)	1.869	(7)	Ga–N(1A)	2.000	(6)
Si–N(1)	1.823	(7)	Si–N(2)	1.697	(8)
Si–C(9)	1.891	(11)	Si–C(10)	1.876	(13)
N(1)–C(1)	1.571	(10)	N(2)–C(5)	1.490	(13)
C(1)–C(2)	1.515	(14)	C(1)–C(3)	1.493	(16)
C(1)–C(4)	1.540	(14)	C(5)–C(6)	1.497	(15)
C(5)–C(7)	1.536	(14)	C(5)–C(8)	1.508	(16)

Bond Angles (°) for 2

Cl–Ga–N(1)	125.3(2)	Cl–Ga–N(2)	114.2(3)
N(1)–Ga–N(2)	81.2(3)	Cl–Ga–N(1A)	116.7(2)
N(1)–Ga–N(1A)	89.9(2)	N(2)–Ga–N(1A)	122.7(3)
N(1)–Si–N(2)	93.1(3)	N(1)–Si–C(9)	119.7(4)
N(2)–Si–C(9)	116.0(5)	N(1)–Si–C(10)	113.7(4)
N(2)–Si–C(10)	116.2(4)	C(9)–Si–C(10)	99.4(5)
Ga–N(1)–Si	87.6(3)	Ga–N(1)–C(1)	121.3(6)
Si–N(1)–C(1)	118.7(5)	Ga–N(1)–GaA	90.1(2)
Si–N(1)–GaA	118.8(3)	C(1)–N(1)–GaA	114.2(5)
Ga–N(2)–Si	97.7(4)	Ga–N(2)–C(5)	130.2(6)
Si–N(2)–C(5)	130.9(6)	N(1)–C(1)–C(2)	110.4(6)
N(1)–C(1)–C(3)	109.0(8)	C(2)–C(1)–C(3)	111.4(9)
N(1)–C(1)–C(4)	109.7(8)	C(2)–C(1)–C(4)	104.7(9)
C(3)–C(1)–C(4)	111.4(8)	N(2)–C(5)–C(6)	110.7(8)
N(2)–C(5)–C(7)	109.2(8)	C(6)–C(5)–C(7)	109.5(10)
N(2)–C(5)–C(8)	110.7(10)	C(6)–C(5)–C(8)	107.6(9)
C(7)–C(5)–C(8)	108.9(9)		

TABLE III
Bond lengths and bond angles in 3

Bond Lengths (Å)

Ga-Cl	2.159 (4)	Ga-N(2)	2.113 (7)
Ga-N(3)	1.902 (7)	Ga-N(4)	1.909 (7)
Si(1)-N(1)	1.748 (8)	Si(1)-N(2)	1.803 (8)
Si(1)-N(3)	1.695 (8)	Si(1)-C(17)	1.855 (8)
Si(2)-N(1)	1.759 (8)	Si(2)-N(2)	1.819 (7)
Si(2)-N(4)	1.709 (7)	Si(2)-C(18)	1.821 (12)
N(1)-C(1)	1.479 (14)	N(2)-C(5)	1.438 (14)
N(3)-C(9)	1.477 (13)	N(4)-C(13)	1.463 (10)
C(1)-C(2)	1.546 (16)	C(1)-C(3)	1.486 (15)
C(1)-C(4)	1.527 (14)	C(5)-C(6)	1.517 (14)
C(5)-C(7)	1.538 (15)	C(5)-C(8)	1.526 (15)
C(9)-C(10)	1.505 (14)	C(9)-C(11)	1.500 (15)
C(9)-C(12)	1.525 (16)	C(13)-C(14)	1.512 (18)
C(13)-C(15)	1.506 (18)	C(13)-C(18)	1.508 (17)

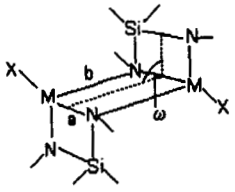
Bond Angles (°)

Cl-Ga-N(2)	125.1(2)	Cl-Ga-N(3)	119.9(2)
N(2)-Ga-N(3)	79.7(3)	N(2)-Ga-N(4)	79.5(3)
N(3)-Ga-N(4)	117.8(3)	N(1)-Si(1)-N(2)	85.4(4)
N(1)-Si(1)-N(3)	116.9(3)	N(2)-Si(1)-N(3)	94.9(4)
N(1)-Si(1)-C(17)	115.5(4)	N(2)-Si(1)-C(17)	120.9(4)
N(3)-Si(1)-C(17)	117.5(4)	N(1)-Si(2)-N(2)	84.6(3)
N(1)-Si(2)-N(4)	116.4(4)	N(2)-Si(2)-N(4)	93.8(3)
N(1)-Si(2)-C(18)	116.5(5)	N(2)-Si(2)-C(18)	121.0(5)
N(4)-Si(2)-C(18)	118.0(4)	Si(1)-N(1)-Si(2)	95.0(4)
Si(1)-N(1)-C(1)	130.3(6)	Si(2)-N(1)-C(1)	129.5(5)
Ga-N(2)-Si(1)	85.4(3)	Ga-N(2)-Si(2)	86.0(3)
Si(1)-N(2)-Si(2)	91.1(4)	Ga-N(2)-C(5)	120.5(6)
Si(1)-N(2)-C(5)	129.9(5)	Si(2)-N(2)-C(5)	129.4(6)
Ga-N(3)-Si(1)	95.4(4)	Ga-N(3)-C(9)	126.3(5)
Si(1)-N(3)-C(9)	137.3(6)	Ga-N(4)-Si(2)	96.0(3)
Ga-N(4)-C(13)	127.0(6)	Si(2)-N(4)-C(13)	136.7(7)
N(1)-C(1)-C(2)	110.9(8)	N(1)-C(1)-C(3)	109.9(10)
C(2)-C(1)-C(3)	108.9(9)	N(1)-C(1)-C(4)	110.1(8)
C(2)-C(1)-C(4)	107.7(10)	C(3)-C(1)-C(4)	109.4(9)
N(2)-C(5)-C(6)	110.0(9)	N(2)-C(5)-C(7)	109.5(9)
C(6)-C(5)-C(7)	109.7(8)	N(2)-C(5)-C(8)	109.7(8)
C(6)-C(5)-C(8)	108.8(10)	C(7)-C(5)-C(8)	109.2(9)
N(3)-C(9)-C(10)	109.8(8)	N(3)-C(9)-C(11)	110.4(8)
C(10)-C(9)-C(11)	110.4(10)	N(3)-C(9)-C(12)	109.5(10)
C(10)-C(9)-C(12)	107.7(9)	C(11)-C(9)-C(12)	108.9(9)
N(4)-C(13)-C(14)	109.8(8)	N(4)-C(13)-C(15)	109.3(9)
C(14)-C(13)-C(15)	112.1(10)	N(4)-C(13)-C(18)	110.5(8)
C(14)-C(13)-C(18)	107.9(11)	C(15)-C(13)-C(18)	107.2(9)

In Figure 3 the molecular structure of **3** is displayed. Compared to the methyl derivative $(MeSi)_2(NtBu)_4Ga\text{-}Me$[6] the chloro compound **3** has very similar molecular dimensions with the exception of the bonds adjacent to gallium. As in **2** (compared to **1**) the gallium atom in **3** is more positively charged than in the corresponding methyl derivative. This is reflected by shorter Ga—N distances in **3** [Ga—N (3, 4) = 1.909(7) Å, Ga—N (2) 2.113(7) Å] compared to those in the methyl derivative [1.929(3) Å and 2.119(3) Å respectively].[6]

TABLE IV

Correlation of bond lengths (Å), interplanar angles (°) and estimated group electronegativities[18] in ring systems $[X\text{-}MN(t\text{Bu})N(t\text{Bu})Si(Me)_2]_2$ of the ladder structure[12,19]



Compound	X-M	a	b	a/b	ω	E.N(group M-X)
$Me_2Si(NtBu)_2Sn$	Sn	2.244(7)	2.389(7)	0.939	105.6	1.8
$Me_2Si(NtBu)_2Ga\text{-}Me$(1)	Ga-Me	2.070(4)	2.060(5)	1.005	115.5	1.6
$Me_2Si(NtBu)_2In\text{-}Me$	In-Me	2.277(4)	2.256(4)	1.009	113.4	1.6
$Me_2Si(NtBu)_2Ga\text{-}Cl$(2)	Ga-Cl	2.054(7)	2.000(6)	1.027	120.7	1.5
$Me_2Si(NtBu)_2Mg \cdot THF$	Mg·THF	2.188(4)	2.112(4)	1.036	123.1	1.3

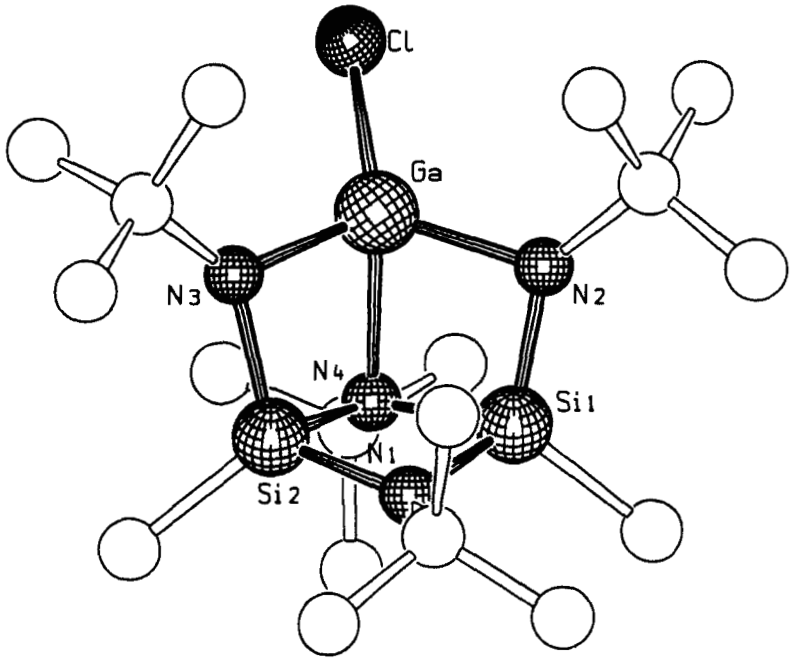


FIGURE 3 Molecular structure of **3**. The carbon atoms are not labeled.

EXPERIMENTAL

Apparatus and Material

All operations were carried out under an atmosphere of dry nitrogen by using a modified Stock vacuum apparatus and Schlenk techniques. ^{1}H NMR spectra were obtained by using Bruker WP 80 (80 MHz) or Bruker WP 200 (200 MHz) instruments. Mass spectra were obtained by using Finnigan MAT 90 (Cl^+) spectrometer. ^{1}H NMR chemical shifts as δ values were measured relative to Me_4Si. Elemental analyses were performed by Beller, Mikronanalytisches Laboratorium, Göttingen, Germany. The compound $Me_2Si(NtBu)_2Sn$[20] was prepared as previously described.

Gallium trichloride was either procured from Aldrich or prepared[21] and was sublimed prior to use. Ga(I)Ga(III)Cl_4 was synthesized by a literature method.[22] Solvents were purified as desribed before.[23,24]

The X-ray crystallographic studies were done by using a Weissenberg camera (Stoe, Darmstadt, Germany) as well as a Siemens automatic four circle diffractometer type AED2. Details of the experimental procedures have been described before.[23]

The details of data collections and structure determinations are summarized in Table I. Final atomic positional parameters as well as the isotropic B values calculated from U_{ij} values have been deposited.[17] Selected bond lengths and bond angles are given in Tables II and III.

Synthesis of the Dimeric 1,3-Di-tert-Butyl-2,2-Dimethyl-4-Methyl-1,3,2,4-Diazasilagalletidine (1)

To a solution of bis(*t*-butylamino)dimethylsilane[25] (1.15 g, 5.7 mol) in hexane (10 mL), a solution of 2.5 M *n*-butyl lithium in hexane (5.6 mL, 11.4 mmol) was added dropwise over a period of 20 min at 20°C with continuous stirring. The mixture was heated under reflux for 2.5 h, stirred further at 20°C for 14 h and then was added dropwise to a solution of gallium trichloride (1.00 g, 5.7 mmol) in diethyl ether (10 mL). The mixture was heated to ca. 50°C for a period of 4 h and stirring was continued overnight. Filtration followed by the removal of the solvent from the filtrate gave a viscous semisolid. Attempts for crystallization at this stage were not successful. The semisolid, after the removal of all solvent was sublimed *in vacuo* (130°C, 0.01 torr). The sublimate was dissolved in a minimum amount of toluene (ca. 5 mL). Compound **1** crystallized from a cooled solution at 0°C during one day. Yield: 0.25 g (12%), m.p. (sealed tube) 145°C, IR(CCl_4): 2959 (vs), 2859 (s), 1458 (s), 1376 (s), 1355 (s), 1251 (s), 1217 (vs), 1095 (s), 1030 (s), 954 (w), 866 (s) and 842 (s) cm^{-1}. ^{1}H NMR (C_6D_6): 1.19 (36 H, $C(CH_3)_3$), 0.46 (12H, $Si(CH_3)_2$), −0.05 (6H, $GaCH_3$). Anal. calc. for $C_{22}H_{34}Ga_2N_4Si_2$: C 46.35, H 9.48, N 9.83. Found: C 45.42, H 9.21, N 9.20.

Synthesis of the Dimeric 1,3-Di-tert-Butyl-2,2-Dimethyl-1,4-Dichloro-1,3,2,4-Diazasilagalletidine (2) *and of 2,4,6,7-Tetra-tert-Butyl-1,3,5-Trimethyl-2,4,6-Triaza-7-Chloro-1,5-Disila-3λ^4-Gallatricyclo[3.1.1.0^{3,7}]-Heptane* (3)

To a solution of 1,3-di-*t*-butyl-2,2-dimethyl-1,3,2,4-λ^2-diazasilastannetidine[20] (2.05 g, 6.6 mmol) in toluene (25 mL), a solution of gallium trichloride (1.16 g, 6.6 mmol) in toluene (25 mL) was added dropwise (20 min) with continuous stirring at 10°C. The mixture was brought to 20°C, stirred further for 36 h and filtered (precipitate: ca. 1.7 g). The filtrate was concentrated to ca. 10 ml *in vacuo* at 40°C and then preserved at 0°C upon which compound **2** deposited as a crystalline mass. This was separated from the mother-liquor by filtration and was found to be essentially pure. Yield: 0.60 g, 30%. Additional quantities of slightly impure material could be obtained by concentrating the mother-liquor (ca. 0.10 g) and also by extracting the precipitate with 10 mL of toluene (ca. 0.05 g) to give a total yield of 0.75 g, 38%. M.p. (sealed tube): 135°C (partial)—156°C (complete). IR ($CHCl_3$): 2964 (vs), 2900 (s), 2865 (s), 1462 (s), 1397 (w), 1386 (w), 1370 (s), 1358 (s), 1197 (s), 1174 (s), 1070 (vs), 1031 (w), 900 (vs), 860 (vs), 815 (s), 766 (vs), 570 (s) cm^{-1}. ^{1}H NMR (C_6D_6): 1.55, 1.35 (36H, $C(CH_3)_3$), 0.81, 0.54 (12H, $Si(CH_3)_2$). Two minor signals at 1.49 ($C(CH_3)_3$) and 0.66 ppm ($Si(CH_3)_2$) with an integral ratio 3:1 were also observed (see text). Anal. Calc. for $C_{20}H_{48}Cl_2Ga_2N_4Si_2$: C 39.31, H 7.86, N 9.17. Found: C 39.54, H 7.96, N 9.23.

The precipitate obtained in the above reaction was heated *in vacuo* (170–180°C, 0.01 torr), the sublimate obtained was dissolved in toluene (10 mL) and filtered to remove a small amount of insoluble material. Most of the solvent was removed from the filtrate to obtain a viscous oil from which crystals of compound **3** appeared after a week. The mother liquor was removed and the crystals were washed with a small quantity of *n*-hexane (0.2 mL). Yield: 0.15 g (5% based on gallium trichloride used). The mother-liquor also showed a significant amount of compound **3**, but no more material of sufficient purity could be obtained. M.p. 205–203° (lit. m.p. 217°C).[7] IR($CHCl_3$): 2963 (vs), 1462 (s), 1356 (s), 1254 (s), 1197 (s), 1096 (s), 1024 (s), 846 (vs), 575 (w) cm^{-1}. ^{1}H NMR (C_6D_6) identical to the one reported before,[7] MS (CT^+) for $C_{18}H_{48}ClGaN_4Si_2$ [M = 475.907] 477, 475 (M^+, ^{37}Cl, ^{35}Cl), 461, 459 [M-CH_3^+].

In a separate experiment, compound **2** was heated *in vacuo* (0.01 torr/160°C). Both the sublimate and the residue showed **3** as a major product (see text).

Reaction of Ga(I)Ga(III)Cl_4 with 1,3-Di-tert-Butyl-2,2-Dimethyl-1,3,2,4-λ²-Diazasilastannetidine

A solution of the stannetidine[20] (0.74 g, 3 mmol) in benzene (10 mL) was added to a solution Ga(I)Ga(III)Cl_4 (0.42 g, 1.5 mmol) at 20°C with continuous stirring (10 min.). The reaction mixture was filtered twice and the solvent was evaporated *in vacuo* to afford a solid mass. ^{1}H NMR (C_6D_6): 1.55, 1.49, 1.35, 1.22, 1.12, 0.82, 0.66, 0.56, 0.54 and 0.38. The integral ratio of compound **2** to other compounds was ca. 3:2. No attempt was made for further analysis.

Synthesis of 1,3-Di-tert-Butyl-2,2-Dimethyl-4-Bis(trimethylsilyl)amido-1,3,2,4-Diazasilagalletidine (**4**)

To a solution of compound **2** (0.24 g, 0.78 mmol) in toluene (10 mL) bis(trimethylsilyl)lithium amide (0.13 g, 0.78 mmol) (prepared from equimolar quantities of hexamethyl disilazane and *n*-butyllithium) in toluene (15 mL) was added all at once. The reaction mixture was stirred for 24 h, filtered and the solvent from the filtrate was removed *in vacuo*. Redissolution in toluene (2 mL) and cooling the solution afforded first a small quantity of unreacted **2** (ca. 0.029 g). The mother-liquor was transferred to another flask and subjected to vacuum sublimation at 100°C/0.01 torr. The sublimate showed the expected ^{1}H NMR spectrum, but the crystals were not suitable for X-ray studies. Yield: 0.229 g (65%), m.p. 70°C. IR ($CHCl_3$): 2954 (vs), 2892 (w), 1456 (w), 1354 (s), 1249 (s), 1064 (vs), 953 (s), 890 (vs), 849 (vs), 618 (w), cm^{-1}. ^{1}H NMR (C_6D_6): 1.27 (18H, $C(CH_3)_3$), 0.40 (6H, $Si(CH_3)_2$), 0.25 (18H, $Si(CH_3)_3$). MS(Cl^+) [M = 430.511]: 430 [M^+], 416, 414 [$M\text{-}CH_3$]$^+$.

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REFERENCES

1. M. Veith, H. Lange, A. Belo and O. Recktenwald, *Chem. Ber.*, **118,** 1600 (1985).
2. M. Hans, Thesis, Universität des Saarlandes, Saarbrücken, 1989.
3. M. Veith and A. Belo, *Z. Naturforsch.*, **42B,** 525 (1987).
4. F. Goffing, Thesis, Universität des Saarlandes, 1987.
5. M. Veith and J. Pöhlmann, *Z. Naturforsch.*, **43B,** 505 (1988).
6. M. Veith, F. Goffing and V. Huch, *Z. Naturforsch.*, **43B,** 846 (1988).
7. M. Veith, F. Goffing, S. Becker and V. Huch, *J. Organomet. Chem.*, **406,** 105 (1991).
8. M. Veith, *Nova Acta Leopoldina*, **264,** 321 (1985).
9. a) W. R. Nutt, R. E. Stimson, M. F. Leopold and B. H. Rubin, *Inorg. Chem.*, **21,** 1909 (1982); b) W. R. Nutt, J. A. Anderson, J. D. Odom, M. M. Williamson and B. H. Rubin, *Inorg. Chem.*, **24,** 159 (1985); c) W. R. Nutt, J. S. Blanton, F. O. Kroh and J. D. Odom, *Inorg. Chem.*, **28,** 2224 (1989); d) W. R. Nutt, J. S. Blanton, A. M. Boccanfuso, L. A. Silks III, A. R. Garber and J. D. Odom, *Inorg. Chem.*, **30,** 4136 (1991).
10. K. C. Kumara Swamy, V. Huch and M. Veith, unpublished data.
11. The methyl exchange could have occurred at an earlier stage also, but since there are several products (^{1}H NMR) in the reaction mixture, a detailed analysis is difficult.
12. a) M. Veith, W. Frank, F. Töllner and H. Lange, *J. Organomet. Chem.*, **326,** 315 (1987); b) M. Veith and B. Bertsch, *Z. Anorg. Allgem. Chem.*, **557,** 7 (1988).
13. The mass spectrum of the aluminium derivative gives molecular ion peak for the dimer, whereas the indium derivative gives for a monomer.
14. M. Veith, H. Lange, O. Recktenwald and W. Frank, *J. Organomet. Chem.*, **294,** 273 (1985).
15. Since methyl exchange can occur between gallium and silicon, many different compositions and structures may come out of this thermolysis.
16. SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc., 1989.
17. Further data for the X-ray structures **1**, **2** and **3** have been deposited at the Fachinformationszentrum (FIZ) Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, and can be ordered on quoting the authors, the journal and the depository number CSD 58473.
18. J. E. Huheey, Anorganische Chemie, Prinzipien von Struktur und Reaktivität, Walter de Gruyter, Berlin 1988, 168.

19. M. Veith, J. Böhnlein, *Chem. Ber.*, **122,** 841 (1989).
20. M. Veith, *Angew. Chem.*, **87,** 287 (1975); *Angew. Chem. Int. Ed. Engl.*, **14,** 263 (1975).
21. W. C. Johnson and C. A. Huskew, *Inorg. Synth.*, **1,** 26 (1939).
22. L. S. Foster, *Inorg. Synth.*, **4,** 111 (1953).
23. M. Veith, J. Fischer, T. R. Prout, M. Nötzel, P. Hobein and V. Huch, *Inorg. Chem.*, **30,** 4130 (1991).
24. D. D. Perrin, W. L. F. Armarego, "Purification of Laboratory Chemicals," 3rd ed., Pergamon Press, Oxford, England, 1988.
25. a) W. Fink, *Helv. Chim. Acta*, **47,** 409 (1964); b) D. J. Brauer, H. Bürger and G. R. Liewald, *J. Organomet. Chem.*, **308,** 119 (1986).